

INDUSTRIAL WASTES

Their Disposal and Treatment

Edited by

WILLEM RUDOLFS

Department of Sanitation

Rutgers University

New Brunswick, N. J.

Contributors

C. S. Baruff	Richard D. Haak
M. Gilbert Burford	Willard W. Hadge
Stuart E. Coburn	Robert P. Logan
Joseph G. DeMann	Joseph W. Masselli
E. F. Eldridge	Robert G. Merman
Harry W. Gehm	Edward W. Moore
W. D. Hatfield	N. H. Sanbarn
H. Heukelekian	Canrad P. Straub

Roy F. Weston



American Chemical Series
Managraph Series

BOOK DIVISION
REINHOLD PUBLISHING CORPORATION.

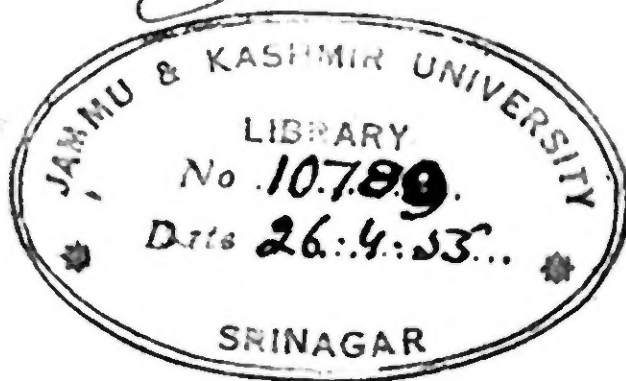
Advertising Management of ACS; Publishers of Chemical Engineering
Catalog, Chemical Materials Catalog and "Materials & Methods."

330 West Forty-Second Street

New York 36, U.S.A

1953

X-S2



ST 01
RGI

COPYRIGHT 1953 BY
REINHOLD PUBLISHING CORPORATION

All rights reserved

Checked

660
R 835I

Library of Congress Catalog No. 52-9792

Printed in the USA

2nd printing April 1954

ATTACHED



GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowl-

edge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical sub-areas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

AMERICAN CHEMICAL SOCIETY

BOARD OF EDITORS

WILLIAM A. HAMOR, *Editor of Monographs*

Associates

L. W. BASS
T. H. CHILTON
FARRINGTON DANIELS
J. BENNETT HILL
E. H. HUNTRESS
C. G. KING

S. C. LIND
C. H. MATHEWSON
LAURENCE L. QUILL
W. T. READ
WALTER A. SCHMIDT
E. R. WEIDLEIN

PREFACE

"Industrial Waste Treatment" has been written by a group of people who are familiar, by virtue of their interests and occupations, with the specific waste treatment and disposal problems. The subject matter is presented critically, with as complete bibliography as considered necessary, without being a compendium or review of the literature. The effluents produced by the various industries have been grouped in a more or less logical manner on the basis of the type of industry or the character of the wastes, and they are discussed in different chapters. The various chapters present the modern views, theories, methods and applications of waste treatment as seen by the collaborators and as practiced in the field. No attempt has been made by the editor to specify the manner of presentation, except that the subjects should be treated from the physical, chemical and biochemical viewpoints, with sufficient engineering features necessary for a comprehensive and authoritative book. The editor feels that he has been particularly fortunate in obtaining contributions from recognized authorities.

A general statement regarding the magnitude and diversity of the industrial waste treatment problem, followed by a chapter dealing with the basic principles involved in stream pollution and self-purification of streams, has been included to illustrate the extent and the physical, chemical and biological effects of industrial wastes on receiving waters, to indicate the fundamental principles involved in industrial waste treatment, and to provide a background for the requirements necessary to treat individual wastes for which no specific methods have been established.

The individual chapters on specific types of wastes reflect the style of the authors. However, in order to provide the necessary continuity the authors have followed a general pattern, including brief descriptions of the waste-producing processes, sources of wastes, recovery and remedial measures, quantities and characteristics of the wastes, methods of treatment, and in several instances, the effect of the wastes on domestic sewage treatment processes.

The book was planned to present a series of contributions which would be welcomed by engineers and chemists in industry confronted with waste treatment problems, by research workers in the field, by teachers and students, by executives in industry who need to familiarize themselves with the proper treatment and disposal of wastes, and by those govern-

ment, state and municipal officials who are called upon to evolve policies for development and control, as well as municipal employees charged with treatment of domestic sewage and industrial wastes.

The editor wishes to express appreciation to all those who have helped to make this book possible.

WILLEM RUDOLFS

New Brunswick, N. J.
February, 1953

CONTENTS

PREFACE	v
<i>Chapter</i>	<i>Page</i>
1. THE PROBLEM, <i>Willem Rudolfs</i>	1
2. STREAM POLLUTION AND SELF-PURIFICATION, <i>H. Heukelekian</i>	8
3. MILK PRODUCTS WASTE, <i>E. F. Eldridge</i>	31
4. CANNING, FREEZING AND DEHYDRATION, <i>N. H. Sanborn</i>	51
5. SLAUGHTERHOUSE AND MEAT PACKING WASTES, <i>Willem Rudolfs</i>	87
6. THE FERMENTATION INDUSTRIES, <i>C. S. Boruff</i>	99
7. CORN STARCH PROCESSES, <i>W. D. Hatfield</i>	132
8. WASTES FROM THE TANNING, FAT PROCESSING, AND LAUNDRY SOAP INDUSTRIES, <i>Edward W. Moore</i>	141
9. TEXTILE DYEING AND FINISHING, <i>Stuart E. Coburn</i>	171
10. PULP, PAPER AND PAPERBOARD, <i>Harry W. Gehm</i>	194
11. ACID AND EXPLOSIVES WASTES, <i>Robert P. Logan</i>	232
12. STEEL PICKLING, <i>Richard D. Hoak</i>	255
13. PLATING WASTES, <i>M. Gilbert Burford and Joseph W. Masselli</i>	283
14. WASTE DISPOSAL PROBLEMS IN THE MINING, PREPARATION AND CARBONIZATION OF COAL, <i>Willard W. Hodge</i>	312
15. WATER DISPOSAL PROBLEMS OF THE PETROLEUM INDUSTRY, <i>Roy F. Weston, Robert G. Merman and Joseph G. DeMann</i>	419
16. TREATMENT AND DISPOSAL OF LIQUID RADIOACTIVE WASTES, <i>Conrad P. Straub</i>	450
17. MISCELLANEOUS WASTES, <i>Willem Rudolfs</i>	471
INDEX	487

1. The Problem

Willem Rudolfs

Department of Sanitation, Rutgers University, New Brunswick, N.J.

KINDS OF INDUSTRIAL WASTE

Water is an invaluable natural resource. The importance of industrial waste discharges in relation to water supply and water use is not the same in different parts of the country, nor is it equally great in specific sections; the problem varies within a specific area, depending upon the distribution and type of industry. Before the advent of process water treatment the location of many specific types of "wet" industries was determined as much or more by the character and quantity of water available as by the presence of raw materials, labor, transportation and markets.

Although there are areas in which a variety of industrial wastes is produced, there is a considerable concentration of industries in certain parts of the country yielding similar types of wastes. For instance, the textile industry, concentrated in New England and North Carolina, presents different problems from the petroleum industry with refineries in the East and oil fields in the West. The canning industry is more widespread, but has intensified problems in the Middle West, California and Florida. The dairy industry is represented by many small plants located in agricultural areas and along small streams. Waste problems from paper and pulp production in Maine, the Northwest and South are considerable, but the industries are located in more or less restricted areas. The waste from paper making is found in many states, although about half the paper and paperboard production is located in the South. Metal wastes (steel pickling) in Pennsylvania and Illinois and metal plating wastes in Connecticut and New Jersey require different methods of treatment from wastes of the chemical and pharmaceutical industries in New York, New Jersey, and Pennsylvania. Fermentation wastes, including alcohol, beer, yeast and antibiotics, are restricted to certain definite areas, whereas wastes from power laundries are generally distributed. The problem of industrial wastes and their treatment is affected by the volumes of dilution

water available and the permissible use of streams. In general, the more densely the area is populated the greater the problem of industrial waste treatment and disposal.

The volume of wastes produced varies with the industry and also within each industry. This is indicated by the estimated water consumption of a number of selected industries⁵ which produce appreciable quantities of liquid wastes (Table 1).

TABLE 1

Industry	Number Establish- ments	Units	Gals Per Unit	Mil. Gals (1947)
Steel (finished)	419	tons	65,000	4,020,721
Oil refining	437	bbl	770	1,453,675
Gasoline	—	bbl	357	791,325
Wood pulp:				
Sulfate		tons	64,000	342,829
Sulfite	226	tons	60,000	167,758
Soda		tons	85,000	41,784
Groundwood		tons	5,000	10,249
Paper	665	tons	39,000	415,226
Paperboard		tons	15,000	137,802
Coke	167	tons	3,600	284,493
Beer	440	bbl	470	41,373
Whiskey	226	gal	80	21,155
Milk, cream, butter	—	lb	0.11-0.25	12,286
Canning and preserving	2,265	cases	7.5 -250	8,520+
Woolens and worsted fabrics	495	lb.	70	3,252
Wool scouring	74	lb	1.26	2,648
Tanning	561	lb	8	1,910
Soap	249	lb	0.25	1,034
Meat packing, hogs	2,153	hogs	11	568
Cane sugar refining	25	tons	1,000	358
Rayon, all types	38	lb	0.16	119

Aside from the variations in the types of industrial wastes and the uneven distribution of the industries, the magnitude of the problem is rarely realized. According to surveys made by the U.S. Public Health Service,⁶ the organic pollution contributed by the industries in the Ohio River Valley is about equal to the pollution contributed by the entire population. In industrial states such as New Jersey, with some 2,000 industries producing liquid wastes, the waste volume is equal to that of the entire sewered population of the state, but the population equivalent is greater. In Tennessee, industrial wastes are reported to have a pollutional effect on the streams equivalent to approximately 1.35 times that produced by the population discharging domestic sewage into the streams.⁷ Certain rivers or sections of rivers are subjected to volumes and con-

centrations of wastes far beyond the raw sewage population equivalents. The following two examples illustrate this point.

The Androscoggin River in the region of Lewiston and Auburn, Maine, receives the municipal sewage from a summer population of 38,000, the sulfate waste liquor with a population equivalent of 1,500,000 and other wastes totaling 150,000 population equivalent.² The lower Raritan River in New Jersey receives the treated sewage of about 175,000 people and the partially and untreated wastes, mostly chemical, from a number of industries totaling a population equivalent of about 825,000.⁴

The general relation between pollutorial material originating from industrial wastes and domestic sewage has been estimated by Hoskins¹ and Parran,³ who state that the sewerage systems in the United States serve about 71 million people, of which approximately 40 per cent discharge untreated sewage directly into the streams. They estimate that the organic industrial wastes discharged into the same streams was equivalent to 55 to 60 million people. These estimates indicate that at least half the total pollutorial load carried by streams and water courses is caused by industrial wastes. These estimates do not include discharged wastes which are considered to have no biochemical oxygen demand, those which affect the stream household on account of poisonous substances, cause deposits in streams which may interfere with bottom organisms (fish food), those which cause a change in the chemical composition of water (brines, acids), or those which may interfere with fish life or recreation (fibers, oils).

On the basis of the latest available information, the average daily population equivalents of the more important oxygen-demanding wastes produced by groups of industries in the United States during 1949 are as estimated in Table 2.

TABLE 2

Industry	Population Equivalent in Millions
Paper, pulp, board	43.6
Fermentation (aleohol, beer, wine, yeast, antibiotics)	29.7
Packing and slaughterhouse	12.5
Textile, dyeing	9.9
Canning and freezing	9.3
Beet sugar	17.0
Petroleum refining	3.5
Miscellaneous (synthetic rubber, tannery, soap, fat processing)	4.7
	<hr/> 134.4

In addition, a large number of industries, including pharmaceu-

tial, dyes, and power laundries, discharge wastes containing putrescible materials.

Furthermore, inorganic wastes, acids, alkalies, oils and brines are discharged in large quantities. For instance, during 1949 about 11 million tons of sulfuric acid were produced in addition to other acids such as nitric and hydrochloric. Most of these acids are discharged as wastes. In addition the mine drainage from soft (bituminous) coal amounts to only some 2,500,000 tons a year calculated as concentrated sulfuric acid.

It is estimated that about 60 per cent of the domestic sewage discharged into sewerage systems is partially or completely treated. A considerable portion of the industrial wastes is also treated to various degrees, either separately or in combination with domestic sewage. No reliable statistics are available to estimate the reduction of industrial pollutional matter by treatment, but on the assumption that half of the pollutional material is removed, it is evident that the industrial waste treatment problem is of greater magnitude than the domestic sewage treatment problem.

With increasing density of population and industrial expansion the need for treatment and disposal of waste has grown. Domestic sewage treatment plants have increased from about 2,700 in 1928 to nearly 6,000 in 1945.⁷ Although no complete survey is available regarding the number of industrial waste treatment plants, it is not likely that a similar increase in facilities has taken place to treat industrial wastes, although many industries discharge their wastes in municipal sewers and sewage treatment plants. Sportsmen, commercial fisheries, health and similar organizations have become more active in combating pollution by industrial wastes. Many industrial committees, councils, and institutes have been established during the last few years to study, disseminate information, develop research projects and operate pilot installations for specific types of wastes common to the particular industries. Among those most active are the cannery, dairy, paper and pulp, steel and chemical industries.

Legislation to regulate the discharge of wastes and abate pollution by compulsion has been enacted by the federal government after nearly 50 years of debate. In 46 states more or less effective laws and regulations are in force. The state laws can be divided into two groups: (1) laws which establish a state agency, which formulate and enforce certain regulations, and (2) laws defining pollution, stating that wastes may not be discharged and establishing penalties. Municipal ordinances are mostly confined to control the discharges and indicate necessary pre-treatment. In addition, there are authorities, commissions, and compacts, which may control groups of municipalities, sections of one or several states, parts of river systems or entire drainage areas.

TREATMENT OF INDUSTRIAL WASTES

New and Existing Locations

The policy of many of the larger companies is to investigate, in addition to many other factors, the local pollution control requirements, study conditions and flow of receiving waters at the locations under consideration, determine the available diluting water, prepare and describe plans and specifications for treatment facilities to meet local requirements, and obtain formal approval of treatment works from the pollution control authorities.

Because many industrial plants have been in operation without adequate consideration of waste treatment and disposal, it is of primary importance to consider the possibility of modification of the processes to change the character and reduce the quantity of waste.

Reduction of Waste

Reduction of wastes may frequently be accomplished by closer supervision of the processes or good housekeeping. Provision of adequate assistance and funds for sampling and analysis to obtain basic data may lead to segregation of wastes to simplify treatment procedures, to prevent undesirable interaction of wastes, to avoid difficulties, and provide information for the construction and operation of waste treatment plants.

Re-use and Recovery of By-products

The possibility of re-use of wastes in the processes, for washing or cooling water purposes, may be attractive for waste volume reduction. Under certain conditions, a reduction in the volume of wastes does not reduce the quantity of pollutorial matter, but the more concentrated waste may conceivably be treated at lower construction and operating cost.

By-product recovery is of interest in those industries where the products are valuable and salable. This is particularly the case in the food and fermentation industries. During times of stress or war, the recovery of by-products may be financially feasible and attractive, such as grease recovery from wool scouring and alcohol production from paper waste, but recovery of by-products from waste is usually unprofitable. Sometimes the revenue from by-product recovery may pay in part for the cost of treatment of the remaining waste. Frequently, the recovery of by-products produces new waste problems, which may be equally undesirable or even worse than the original ones.

Treatment—A Part of Production

Industrial waste treatment should be considered as an integral part of production. Waste treatment must be considered in research, design, pilot

plant, and full scale operation. Large companies may have a vice-president in charge to direct, coordinate, and integrate a proper program of waste reduction and treatment with production. Employment of a competent waste disposal specialist, whose duties and powers are clearly defined, is necessary. Such a specialist requires help and equipment to perform his functions properly. Smaller companies usually employ outside specialists to help solve the problem.

All responsible, progressive and law abiding companies are interested in abating pollution and avoiding misuses of water courses. Their problem is to properly integrate waste treatment with production and to construct and maintain efficient treatment devices at the lowest possible cost.

Basic Principles of Treatment

The principles of industrial waste treatment are based upon:

- (1) Separation of solids from the liquid.
- (2) Oxidation of organic and oxygen demanding materials.
- (3) Neutralization.
- (4) Removal of poisonous substances.
- (5) Disposal of residues.

The methods used are physical, chemical and biological in nature or may constitute combinations of various methods. The methods used for separation of solids from the liquid are confined, in most instances, to removal of suspended solids by screening and sedimentation. In specific instances centrifuges and flotation processes are employed. The removal of soluble and suspended solids may be enhanced by the application of coagulants and precipitants.

Oxidation of organic materials is accomplished by biological methods. Aeration alone may have some value when volatile substances are present, but it is rarely sufficient or effective.

Large volumes of waste requiring neutralization are acid in character. Neutralization with lime, sodium hydroxide, sodium carbonate, or combinations of neutralization agents commonly employed, usually requires equalization for economy and control. Neutralization of alkaline wastes with sulfuric acid, carbon dioxide, sulfur dioxide or flue gases is carried out under certain conditions. The problem of sludge formation and disposal is of considerable importance in all neutralization procedures.

Removal of poisonous substances requires specific methods of treatment, depending upon the type and amount of poisonous material present. As far as metallic ions are concerned the specific methods are, as a rule, chemical in nature, whereas wastes containing organic poisons, antiseptics and similar materials may be amenable to biological treatment. Solvents.

in general, can be treated in low concentrations biologically with other wastes, but since many of the solvents have a high oxygen demand, stripping or recovery may be cheaper than biological treatment.

Residues produced by treatment of industrial wastes vary from thin slurries to precipitates and cakes ranging in moisture content from 50 to 90 per cent. Disposal of the residues depends upon the character of the materials. Those consisting primarily of organic matter may be dried and incinerated; others may be used for fill or placed on dumps. Each residue is a problem in itself and methods of waste treatment selected must take into consideration proper and economical disposal of sludge.

References

1. Hoskins, *Sewage Works Engineering*, **17**, 493 (1945).
2. Lawrance, W. A., *Sewage Works J.*, **20**, 881 (1948).
3. Parran, T., *Ind. Eng. Chem.*, **39**, 560 (1947).
4. Rudolfs, W., and Fletcher, A. H., "Rept. on Pollution of Raritan River and Bay," Middlesex County Sewerage Authority (1951).
5. Task Committee No. 1, The Water Policy Panel, Engineers Joint Council (June 1950).
6. U.S. Public Health Service, "Ohio River Pollution Survey," Cincinnati (1942).
7. U.S. Public Health Service, "Inventory of Water and Sewage Facilities in the United States," Cincinnati (1948).

2. Stream Pollution and Self-Purification

H. Heukelekian

Department of Sanitation, Rutgers University, New Brunswick, N.J.

The effect of discharge of sewage and industrial wastes should be considered from two interrelated standpoints: (a) the effect of wastes on the stream environment, and (b) the effect of the stream on the wastes. The first may be considered as pollution effects and the second as self-purification.

EFFECTS OF POLLUTION ON THE QUALITY OF SURFACE WATERS

Pollution by Sewage

Pollution by sewage contributes organic and inorganic materials and large numbers of bacteria, all of which have an objectionable effect on the quality of the water in the stream and its usage for domestic and industrial purposes. The inorganic matter in sewage is in suspension and in solution. The suspended matter (sand, grit, ashes) is of importance only in relation to sludge deposits. The soluble substances affect the chemical composition of the water. The organic matter is present in coarse or fine suspension or in solution and is composed primarily of carbohydrates, fats and proteins. The coarse, and a portion of the finely divided materials, settle more or less rapidly to the stream bed forming sludge deposits. The oils and fats spread on the surface of the water forming unsightly slick, while the remainder of the materials remain in suspension (depending on the velocity of the stream) and are acted upon in transit by micro-organisms.

The effects of sewage pollution on the quality of the water may be physical, chemical and biological.

Physical Effects. The finely divided matter in sewage imparts turbidity and increases the suspended solids content of the water, makes the stream esthetically objectionable and increases the cost of treatment for domestic and industrial purposes. Suspended solids render the water unfit for process

waters, boilers, condensers and creates fouling of tubes and pipes unless properly treated.

Tastes and odors are imparted to the water by sewage either directly or indirectly. Hydrogen sulfide may be present in sewage or may be produced as a result of biological activity in the stream from the reduction of sulfate or organic sulfur compounds. Sludge deposits exposed at low water or under certain conditions in a submerged state are particular sources of odor.

Chemical Effects. The chemical composition of surface waters is altered appreciably by the discharge of sewage. The total salt content may be increased. An increase in chloride content is objectionable to domestic water supply; sulfates are objectionable from the standpoint of boiler waters and as a source of hydrogen sulfide production under anaerobic conditions. The ammonia nitrogen contained in sewage tends to increase the concentration of this constituent in the water. Nitrates discharged with oxidized effluents and nitrates produced in the stream from the ammonia nitrogen stimulate the growth of algae in the water causing an indirect increase in tastes and odors and in some cases resulting in actual nuisances as a result of decomposition of large quantities of organic matter accumulated by the growth of these organisms.

The organic matter contained in sewage modifies the chemical composition of the water directly and indirectly. Directly, an increase in the organic matter of the water causes an increase in the turbidity. The indirect effects of organic matter on biochemical processes are discussed below.

Bacterial Pollution. Unpolluted stream water has low bacterial numbers. Part of the natural bacterial population consists of coliform organisms which are derived from run off from fields and soil and are similar to the coliform organisms derived from sewage. The balance of the flora consists of bacteria native to the water and is specially adapted to grow under the environmental conditions prevailing in the stream. It is doubtful whether many of the native bacteria are actually grown or counted in ordinary culture media. They are adapted to grow in a water environment of low food content by attaching themselves to inert surfaces forming slimy growths and deriving their food by adsorption on biological surfaces.

Sewage greatly increases the density of pollutional bacteria (coliform) in water. The daily per capita discharge of coliform organisms in sewage has been estimated at 100 to 400 billions. In addition there may or may not be present certain pathogenic organisms such as typhoid or dysentery bacteria. Generally, neither the pathogenic nor the pollutional forms of bacteria multiply in the water, although some initial increase in the numbers of coliform organisms has been noted below a point of sewage discharge. It is logical to expect that the numbers of native water bacteria

increase greatly in response to the addition of food materials present in sewage. With increasing time of flow the pollutorial forms decrease in number, as well as the native population, because of the exhaustion of food. Depending, therefore, on the distance of intake point from the source of pollution, water will contain variable numbers of bacteria. It has been shown by Streeter⁵ that for domestic supply a raw water containing coliform organisms in density greater than 5,000 per 100 ml cannot be adequately treated by the ordinary process of coagulation, filtration and chlorination. A water heavily contaminated with bacteria of either pollutorial or native forms is unsuitable for cooling purposes and as process waters without sterilization and treatment because of slime formation. Bacterial pollution of surface waters also endangers the harvesting of shellfish and use of bathing places.

Other Biological Forms. As a result of sewage pollution the numbers of protozoa increase in the water. Some of these organisms feed on bacteria and help keep their numbers down and thereby increase their biochemical activities. The numbers of filamentous organisms, such as *Sphaerotilus* and *Leptomitius*, increase and attach themselves in long strands to sticks and stones and float downstream below sewer outfalls. Certain forms of filamentous algae such as blue greens and *Spirogyra* will also be found attached in the same environments as the filamentous bacteria, in coves and on the surface. As the stream recovers itself from the pollution the numbers and types of green algae increase.

A number of higher animals, such as rat-tail maggots, *Tubifex* (sludge worms) and *Chironomous* (blood worms) are found in sludge deposits.

Pollution by Industrial Wastes

Physical Effects. Many industrial wastes have similar effects on the turbidity of the water as sewage. The turbidity imparted to water by industrial wastes may be organic or inorganic in nature. Examples of the latter type of turbidity are muds from drilling operations and coal wash-eries. With few exceptions most industrial wastes impart organic suspended matter and increase the turbidity of water.

Many industrial wastes are highly colored, and are still detectable after high dilution. Wastes from dye manufacturing plants, textile wastes, wood and flax cooking wastes, fermentation wastes and pickling liquor wastes are particularly objectionable from the standpoint of color.

Taste and odor producing substances such as phenols, gas and by-product coke manufacturing wastes, oil and petroleum wastes, munition manufacturing wastes, sulfides, etc., make the water unfit for domestic consumption or require expensive treatment processes for their removal. Aside from these direct effects, tastes and odors are produced indirectly

as a result of bacterial decomposition of organic industrial wastes as well as by algae.

Chemical Effects. Acid and alkaline wastes may change the pH value of the stream to the extent of interfering with the self-purification processes and rendering the water corrosive for industrial and boiler usages or increasing the hardness. Wastes from chemical manufacturing plants, acid mine drainage and pickling liquor wastes have deleterious effects in all these respects. The chloride content of the water is increased by the discharge of oil drilling operations.

The discharge of toxic materials, such as cyanides, and chromates affects the self-purification capacity of the stream and renders it unfit for drinking purposes. The effect of certain organic wastes as intestinal irritants is only vaguely understood.

Bacterial Pollution. Industrial wastes, in general, do not contain pathogenic bacteria with the possible exception of anthrax organisms found in tannery wastes and, therefore, their direct effect on bacterial quality of water is not important. Neither do they contribute large numbers of intestinal organisms of the coliform type. The effect of industrial wastes on bacterial population is indirect, produced as a result of the multiplication of the bacteria deriving their food from the organic matter or the destruction of bacteria by toxic materials present in the waste.

SELF-PURIFICATION

Agencies of Self-purification

The discharge of sewage and wastes sets in motion a complex chain of physical, chemical, biological and biochemical events, the net result of which is the ultimate elimination of the pollution. The process is collectively designated as self-purification.

In the course of years, and as a result of numerous investigations, a general concept of the nature of the self-purification process resulting from sewage pollution has been obtained. The detailed nature of the reactions and interactions and the definite rates of self-purification in streams of various characteristics are still not entirely understood.

Physiological Activity of Bacteria. The most important phase of self-purification is the result of bacterial action upon the pollution material. It is therefore necessary to understand the general nature of bacterial processes and metabolism. Bacteria bring about profound changes in the physical and chemical nature of their environment, but are also affected in turn by them. The changes brought about by bacteria in their environment are the result of their life activity, which is collectively referred to as

metabolism. Metabolism consists of the related processes catabolism or dissimilation and anabolism, synthesis or assimilation. The catabolic process takes place after the food enters the cell and material is broken down with the liberation of energy. Where the food is of such a nature that it cannot diffuse and enter the cell bacteria excrete enzymes to hydrolyze it and convert it to more readily diffusible form. The hydrolytic reactions taking place outside the cell by means of exoenzymes liberate only small amounts of energy which in no way can be made use of directly in the cellular metabolism. Metabolism starts, therefore, after the food materials enter the cell. The materials are broken down by means of endoenzymes with the liberation of energy. Certain fractions of the catabolic products are then used for the synthetic reactions of the bacteria, building up their cellular materials by utilizing the energy liberated in the catabolic processes. It follows that the energy liberated in the catabolic processes must be greater than the amount of energy required for synthetic processes for the building of the complex materials from the building blocks produced in the catabolic processes. If the energy produced is in excess of that required for synthetic purposes, the balance may be dissipated into the surrounding environment as heat, which under certain favorable conditions may be registered as a rise in the temperature of the surrounding medium. Such conditions prevail when an excess of highly oxidizable organic matter is placed in open, well ventilated piles, such as in manure, hay or partially dehydrated sludge and garbage heaps. Temperature under such favorable conditions may be raised to as high as 140 to 180° F. The breakdown of food and the growth of bacteria are closely related to each other. There is no growth without food and there is a relationship between the amount of food utilized and the quantity of growth made.

Catabolic dissimilation of food may take place either under anaerobic or aerobic conditions. Under anaerobic conditions the food materials are broken down incompletely to various intermediate compounds in which most of the energy of the initial material still remains. It follows, therefore, that the quantity of growth made under anaerobic conditions will be smaller than under aerobic conditions. Of greater importance is the nature of the intermediate products formed. Various organic acids such as acetic, butyric, propionic, valeric, lactic as well as lower alcohols—ethyl, butyl, propyl, etc., are formed from carbohydrates, fats and proteins. The products of the degradation of nitrogenous materials are amino acids and ammonia. The gases formed are primarily methane, hydrogen, carbon dioxide and hydrogen sulfide.

Under aerobic conditions the decomposition of food materials is complete; all the energy locked up in the food materials is liberated resulting

in greater bacterial growth. The end products are carbon dioxide, water, ammonia, and nitrates, none of which create offensive conditions.

Energy liberation under both aerobic and anaerobic conditions is the result of a series of steps involving the dehydrogenation of the organic materials. Under aerobic conditions oxygen serves as a hydrogen acceptor. Under anaerobic conditions energy liberation as a result of dehydrogenation of the organic materials may take place by: (a) intermolecular respiration in which oxygen rich compounds such as nitrates, sulfates and carbon dioxide serve as hydrogen acceptors, or (b) intramolecular respiration in which the hydrogen donor and acceptor are within the same molecule and hydrogenation proceeds by rearrangement of hydrogen atoms, whereby one part of the molecule is oxidized (dehydrogenated) and another part, which receives the hydrogen atoms, is reduced.

All three types of energy-liberating reactions take place in the stream. In the presence of dissolved oxygen in the flowing part of the stream, decomposition of food or impurities takes place by a straightforward dehydrogenation of the organic material and hydrogenation or reduction of oxygen. The reaction proceeds by intra- or intermolecular respiration in the flowing part of the stream when oxygen becomes depleted, and in the sludge deposits at all times, except in the superficial layer of sludge in contact with oxygenated water. Which of these two types of reactions will take place in the absence of oxygen depends, among other things, on whether or not external hydrogen acceptors are present. Nitrates may be present in the stream as a result of: (a) surface wash carrying the leachings from the soil, (b) discharge of nitrified effluents from sewage treatment plants, and (c) nitrates produced *in situ* in the well aerated unpolluted section of the stream. In the absence of dissolved oxygen, the oxygen in the nitrates will be utilized by bacteria for the oxidation of the organic matter. The products of nitrate reduction may be nitrates, ammonia or nitrogen gas. Sulfates are present in the stream water naturally or may be added by sewage or industrial wastes. After the nitrites have disappeared, and only after that, will the organisms attack the sulfates in the oxidation of the organic matter. The product of the reduction of sulfate is hydrogen sulfide. In addition sulfide may be produced from the sludge deposits either from sulfates or from organic sulfur compounds.

The utilization of carbon dioxide as a hydrogen acceptor is associated with methane fermentation. This type of fermentation takes place in the sludge deposits of streams. Carbon dioxide may be present in the water as such, or as bicarbonates, or may be produced as a result of other types of bacterial fermentations. The carbon dioxide supply is ample for the progress of methane fermentation under favorable conditions of temperature and seeding.

There are many other types of bacterial fermentations which do not require any external hydrogen acceptors. Examples of this type of reaction are lactic and alcohol fermentation.

All these hydrogenation and dehydrogenation reactions are catalyzed by enzymes which are produced by the bacteria. In addition, there are a great number of enzymes which perform hydrolytic or digestive functions outside the cell, as well as intracellular enzymes which carry on synthetic reactions.

The bacterial cell contains C, H, O, N, S, P and smaller quantities of other elements. It is essential for all of these elements to be present in available form in the medium so that synthetic reactions may proceed and structural requirements be fulfilled. Ordinarily, in the presence of organic material there will be no deficiency of essential food requirements. With the exception of nitrogen and phosphorus, all the other elements are present either in the food material or in the water. In streams polluted with sewage the nitrogen and phosphorus will not be deficient, but with certain industrial wastes of highly carbonaceous nature, the nitrogen and possibly phosphorus may become deficient and thereby restrict the rapid decomposition and stabilization of the organic materials.

The bacterial metabolism associated with the degradation of organic materials is termed heterotrophic metabolism. It is characterized by the utilization of organic materials as a source of energy as well as a source of carbon. It is sharply differentiated from autotrophic metabolism in which the energy is derived from the oxidation of simple inorganic compounds such as ammonia, nitrates, hydrogen sulfide, sulfur, reduced iron, etc., and the carbon is derived from carbon dioxide or bicarbonates. These organisms constitute a small group of highly specialized bacteria which can live in the absence of organic matter and produce organic growths from purely inorganic materials. Autotrophic metabolism can take place only under strict aerobic conditions. The conversion of ammonia to nitrite is brought about autotrophically by a few nitrifying bacteria such as *Nitrococcus* and *Nitrosomonas*, while *Nitrobacter* can only oxidize nitrite to nitrate.

Sulfur bacteria comprise a larger group of organisms, varying from the filamentous forms such as *Beggiatoa* to unicellular forms such as *Thiothrix* and *Thiobacillus thiooxidans*. The complete oxidation of the reduced sulfur compounds results in the production of sulfuric acid. Thus, the production of nitrates and sulfates is the reverse of the reduction reactions of these compounds brought about by two entirely different groups of organisms under different environmental conditions in respect to air supply.

The oxidation of reduced iron compounds is brought about primarily by a group of filamentous bacteria such as *Crenothrix*, *Leptothrix*, *Spiro-*

phyllum and *Galionella*. The action of these organisms under favorable conditions results in the conversion of soluble iron to ferrie hydrate.

Environmental conditions play a very important role in the biochemical reactions, affecting both the nature and rate of the reactions. The far-reaching effects of a change in the oxygen relationship of the environment on the character of the biochemical reactions and the nature of products formed have been discussed above.

The pH value of the surrounding medium has a profound effect on the biological activities. Bacteria cannot grow below a certain pH value. This is known as the minimum pH value which varies with different organisms, some tolerating a greater degree of acidity than others. Generally a pH value of 4.0 is the minimum for most bacteria, although *Thiobacillus thiooxidans*, the sulfur-oxidizing organism mentioned above, is known not only to tolerate but actually prefer pH values below this. It lowers the pH value under favorable conditions to 1.0 as a result of the production of large quantities of sulfuric acid.

As the pH value is increased from the minimum point toward neutrality the rate of bacterial reactions is increased in most cases. The point at which the rate is at a maximum is known as the optimum pH, which for most bacteria will be at or slightly above neutrality. With increasing pH values beyond the optimum the rate of reactions will again drop until it reaches a minimum beyond which no growth can take place. The maximum pH value that can be tolerated for most organisms is 9.0. Self-purification can thus be directly affected by the discharge of alkaline or acid industrial wastes to the streams. The outstanding example in the country is the situation in the upper Ohio River system where large quantities of acids are discharged as a result of acid mine drainage. A number of investigations have shown that the natural purification process is seriously affected; biological life, including plankton and sewage bacteria, is greatly reduced. The inhibition, due to the presence of acids, results in "embalming" the river for that particular stretch and transferring the zone of self-purification further downstream where the acids are neutralized or diluted. Other examples of this nature exist in different localities.

Temperature greatly affects the rate of biological activity. Just as in the case of pH values minimum, maximum and optimum temperature ranges can be recognized. These temperature ranges are not necessarily the same for all bacteria. For example, the cryophilic (cold loving) bacteria have lower temperature requirements for growth than the mesophilic and thermophilic (heat loving) organisms. The latter, with an optimum of 50 to 60°C, are of little importance in streams. The cryophilic organisms, with a temperature optimum of 18 to 20°C, may be found in streams and lakes. The mesophilic organisms have an optimum at a temperature of

20 to 40°C. The rate of activity of these organisms is greatly affected by changes of temperature. The temperature coefficients for biochemical oxidation in streams have been worked out. For every degree rise in temperature within the growth range, the rate of biochemical oxidation increases in the ratio of 1.047. As a result of increased temperature, self-purification and biochemical oxidation of the impurities in a stream are completed in a shorter time because biochemical activities are greater in summer than in winter. With the same quantity of pollution and flow of dilution water in the stream, nuisance conditions will be pronounced in the summer but may not be created in the winter.

Bacteria and their activities are also greatly affected by a number of chemicals such as copper, mercury, chromium, arsenic, phenol, formaldehyde, etc. If these chemicals are present in sufficient quantity the bacteria will be killed and the polluting material will not be biochemically attacked, e.g., self-purification will cease. With lower concentrations of these chemicals the rate of activity may be partially reduced or may be temporarily inhibited. Many industrial wastes contain toxic materials which will affect the stream purification.

Fungi. There are in addition to free-swimming unicellular bacteria a number of filamentous bacteria such as *Sphaerotilus* which because of their filamentous nature are sometimes classified as fungi. Associated with *Sphaerotilus* are a number of filamentous true fungi such as *Leptomitus*. These form dense masses covering stones, and are attached at one end to submerged objects while swaying with the current. They look like cotton wool, but are usually gray in color, and are found in polluted sections below sewer outfalls. They disappear in septic environment when the dissolved oxygen becomes too low. Their method of nutrition is similar to bacteria in so far as they break down complex organic materials to simpler forms.

Photosynthetic Organisms with Pigments. There are a great number and variety of organisms in water with either chlorophyll or other similar photosynthetic pigments. These may be unicellular free-floating, or filamentous and attached forms. Among these are the blue-green and grass-green algae and diatoms. These organisms are able, by means of their pigments, to utilize the sun's energy in synthesizing organic materials from carbon dioxide, water and minerals, and form oxygen. This process is referred to as photosynthesis, and is diametrically opposed to bacterial metabolism in which only the energy contained in chemical compounds is available as a source of energy. Whereas photosynthesis is purely synthetic and results in the formation of organic from inorganic substances, bacterial nutrition is primarily dissimilative and only to a small extent assimilative and therefore requires complex food. The importance of

pigmented organisms in self-purification of streams lies in the fact that under favorable conditions of sunlight and penetration of light into the water they add to the oxygen supply, at times creating a condition of supersaturation. It is difficult to evaluate and to depend upon this source of oxygen, because the production is affected by many variables.

Protozoa. Next to bacteria probably the most important group of organisms contributing to the self-purification of streams are the protozoa. These comprise a group of unicellular animals of a variety of forms such as the amoebae, flagellates and ciliates, and may be either free-floating or attached. Most of them can be more readily differentiated microscopically than bacteria because of their morphological characteristics. The group is also varied physiologically and embraces types with methods of nutrition similar to bacteria and organisms with mouth organs. The latter are able to ingest whole particles like small pieces of suspended organic matter either living (bacteria) or dead. The ingestion of bacteria by some of the protozoa results in appreciable decreases in the numbers of bacteria but not necessarily in a decrease in the rate of activity of bacteria. On the contrary, the remaining bacteria multiply and transform food materials at a greater rate until a maximum population level is reached. The pollutional organic material which was transformed once by the agency of bacteria and partially synthesized into bacterial cells is in turn ingested and digested by the protozoa. These in turn have their enemies in the form of rotifers, water fleas and crustaceans. As the polluted water passes downstream and is purified the organic matter originally present in the pollution is successively attacked and gives rise to the growth of different forms of life until it becomes food for small and large fish. This succession of biological forms helps to differentiate the various zones of pollution and degrees of self-purification.

A different group of organisms are found in the bottom deposits which are perhaps more dependable indicators of stream conditions. Rat-tail maggots can exist in the septic zone and are a sign of extremely polluted conditions. Sludge worms, *Tubifex*, and blood worm (*Chironomus*) larvae are found in sludge deposits where they burrow, ingest and digest large quantities of organic matter and help to stabilize the sludge.

Dilution. Dilution of pollutional wastes might be considered as a phase of self-purification. In certain locations during dry-weather flow the amount of dilution may be inadequate and insignificant. In such cases wastes have to be treated to a higher degree in order to prevent nuisances. There is a very important relationship between the amount of permissible pollutional material discharged and the amount of dilution water available under dry-weather conditions. Proper dispersion of the waste with the dilution water is highly important.

Sedimentation. Sedimentation of suspended matter in wastes results in removal of the part of the pollutional material and its transfer to the bottom deposits where it is acted upon under a different set of conditions. The magnitude of purification obtained by this means will depend upon the percentage of the pollutional material present in suspended form and the velocity of the stream. Additional removals may be obtained as a result of flocculation and coagulation of finely dispersed materials by the chemical constituents of the surface water.

Biochemical Oxidation in Streams

Assay Methods. The biochemical oxygen demand (BOD) test is very valuable from the standpoint of stream pollution and self-purification. It is an empirical test carried on under standardized laboratory conditions simulating the biochemical oxidation in streams. A standard oxygenated dilution water is used for diluting the sewage or waste samples to be tested so that there will be an appreciable and yet not a complete utilization of the dissolved oxygen at the end of a definite incubation period (usually 5 days). The bottles containing the diluted samples are tightly stoppered in order to prevent the solution of additional oxygen from the air during the incubation period. A sufficient quantity of buffer and nutrient elements is added to the dilution water. The organisms, if absent in the sample, are added to the dilution water. If the sample is acid or alkaline it is adjusted to near neutrality before making the dilutions. Where toxic materials are present which interfere with biological life it is not possible to determine the biochemical oxidation and obtain a true value of BOD. In other words, the conditions necessary for proper biochemical oxidations in streams, discussed above, are established. The quantity of dissolved oxygen utilized is measured. (For details of the test see "Standard Methods."⁴)

The quantity of oxygen utilized is a measure of the amount of oxidizable organic matter present in the sample. The rate of oxidation can be determined by measuring the oxygen utilized over a period of 10 to 20 days. A great number of such rate studies have shown that oxidation can be represented by a monomolecular formula as $Lt/L = 10^{-kt}$ in which L is the amount of oxidizable matter present initially and Lt represents the corresponding value at time t and k is a constant. According to this formulation the oxidation of the organic matter is a function of the amount remaining to be oxidized, and the rate of oxidation is constant in terms of material remaining to be oxidized. The k_1 value most commonly used is 0.1 at 20°C, although appreciable variations from the value are obtained. The reaction is between the oxygen in solution and the organic matter, brought about by biological agencies and the results can be expressed

interchangeably either in terms of oxygen utilized or in terms of the amount of oxidizable matter. The influence of other variables such as temperature, pH, seeding, and mineral requirements has been eliminated by the standardized conditions of the test. The greatest amount of oxygen is utilized in the first unit of time and the quantity decreases progressively with each succeeding unit of time until it reaches a constant value. Expressed differently, the oxygen utilized plotted on a semilogarithmic scale against time is a straight line.

After about 10 days of incubation, however, an increase in the rate of oxygen utilization takes place which signifies the start of the nitrification stage (the conversion of ammonia to nitrates); the stage prior to this indicates the oxidation of the organic matter. It is necessary to differentiate between these two stages as far as possible because the oxygen utilized for nitrification is still available in the form of nitrates for oxidation of carbonaceous matter in case the dissolved oxygen disappears. The monomolecular formulation will not apply if nitrification has taken place because the velocity constants of these two stages are entirely different. The BOD values obtained will be higher than for the carbonaceous stage alone and it will be difficult to predict the value for any other time from the observed values or the ultimate demand (L value). Ordinarily, with sewage, nitrification does not interfere during a standard 5-day incubation period, but with materials which have already entered the nitrification stage before the test, oxidation will be primarily of ammonia rather than carbonaceous materials.

The results obtained from the laboratory incubation tests can be used to predict the deoxygenation rates in the stream fairly accurately. There are some variables which make the application hazardous under certain conditions. These are as follows:

(1) The chemical composition of the river water is different than the artificial dilution water used in the laboratory test, although the latter is designed to furnish the necessary nutrient salts for bacterial development and represents the normal ingredients present in surface waters. The concentration of inorganic ingredients in streams varies in different localities. This has led certain workers to use the unpolluted stream water for dilution to determine the specific effect of a waste on a particular stream but the results cannot be compared with other streams.

(2) The influence of proper seeding is difficult to evaluate. Assuming that sewage used as seed has generally the same types of organisms in different localities, it does not follow necessarily that it corresponds to the flora and fauna which are active in biochemical oxidation in a stream receiving a particular waste such as, for example, sulfite liquor or cellulose fiber. It is conceivable that a stream polluted with such wastes develops a highly

specialized flora which brings about the oxidation at a higher rate than can be accomplished in the laboratory with unacclimatized seed.

(3) There is in a stream, in addition to biochemical oxidation, removal of impurities by sedimentation and absorption which is normally not taken into account in the laboratory deoxygenation test and, therefore, the laboratory deoxygenation rates do not correspond to the decrease of BOD in a stream between two points with a time of passage equal to the incubation period in a laboratory test. Even if the test is run after removal of settleable solids, additional removals of solids and BOD take place as a result of flocculation and sedimentation and adsorption of finely divided material on slimy growths occurring in the stream. It has been shown by Kittrell³ that higher deoxygenation constants are obtained in shallow turbulent streams in which the volume of water in relation to the channel area is small as compared with a deep sluggish stream. The difference may be due, in part, to absorption.

A second method of determining deoxygenation and self-purification is based on the rate of decrease of BOD in a stream at successive points separated by known times of flow and assuming that the reduction observed is a measure of oxidation accomplished in the river. This method is subject to the same errors as the projection of the laboratory deoxygenation rates to stream conditions.

A third method is derived by estimating the deoxygenation in a stream on the basis of the algebraic difference between known rates of reaeration and observed rates of change in the dissolved oxygen content of the stream water. This method, commonly referred to as the oxygen sag method, does not involve the direct application of the BOD test and is therefore free from the objections of the two previous methods. It has a disadvantage in that it is difficult to estimate the actual reaeration value of different streams and of different stretches of the same stream. This method will be discussed more fully below.

In all these methods the pollution or dilution contributed by tributary inflow has to be taken into account.

Atmospheric Reaeration

The supply of oxygen in the atmosphere is unlimited but the quantity of oxygen that water can hold in solution is very small. The maximum amount of oxygen that a water can dissolve is referred to as the saturation value which decreases with increasing temperature. Salinity of the water also affects the solubility of the oxygen. Fresh water at 20°C can hold only 9.2 ppm of oxygen. As the dissolved oxygen content decreases below the saturation point more can dissolve and the rate at which it goes in solution increases as the degree of undersaturation increases and is in

direct proportion with the deficit. The solution of oxygen in the surface film of an undersaturated water is instantaneous. Distribution from the oxygen rich layer to the lower layers under quiescent conditions can only take place by diffusion, which is an extremely slow process. Therefore, water under absolutely quiescent conditions, with not even thermal currents, would reaerate very slowly. This slow diffusion rate is increased in nature by a number of factors such as wind action, velocity of flow, thermal currents, and the slope and roughness of the stream bed which cause greater surface agitation. Because the surface film is extremely thin the amount of oxygen that can be supplied at any given time to a deep layer of water, even with mixing and agitation, is extremely small. Thus, reaeration is a function of time and increases with time at a decreasing rate. It is apparent that the reaeration rate in a shallow turbulent stream is higher than in a deep sluggish stream. The rate of reaeration of the underlying body of water is governed primarily by the rate of absorption at the surface of the water, which in turn is determined by the saturation deficit, and secondarily by the temperature, depth and degree of agitation or turbulence.

The measurement of the extent of reaeration in a stream is complicated by many factors. Theoretically, if the actual utilization or deoxygenation between two points in a stream is known, the change in the quantity of dissolved oxygen can be attributed to reaeration. The time of passage of water between the two points, as well as the temperature, must be known. If there is additional pollution or dilution entering between the points, this should be taken into account. The reaeration constant (k_2) is not constant at a given temperature, and even after it is reduced to uniform temperature widely divergent values are obtained for a given section under varying flow conditions. Reaeration constants for any given river stretch can be calculated from the formula $k_2 = CV^n/H_2$, in which c and n are constants associated with the velocity of flow, V is the mean velocity in feet per second, and H is the mean depth of water in feet. If V and H are known, c and n can be obtained by substitution in the formula.

Sag Curve

In a polluted stream deoxygenation will decrease the dissolved oxygen content, whereas reaeration will tend to increase it. The net result of these two opposing processes on the actual dissolved oxygen level of the stream will depend on the quantity of pollution in relation to the stream flow and the rate of reaeration. As the deoxygenation proceeds and lowers the dissolved oxygen level below the saturation value more oxygen will go in solution at a rate which increases with the deficit. The deficit will depend

on the initial load of BOD and on the rate at which the oxygen demand is satisfied. Initially, below the source of pollution, the rate at which the demand is exerted is greatest. Under these conditions the reaeration may not be able to cope with the demand and the dissolved oxygen level drops. The magnitude of the drop depends on the pollution load and rate of reaeration. It may reach a value of zero if these two factors are unfavorable. With increasing passage time the oxygen demand exerted decreases as the residual oxygen demand diminishes as a result of biochemical activities. At this point the trend of dissolved oxygen will be upward as the reaeration rate counterbalances the effect of decreased deoxygenation. However, the rate at which dissolved oxygen increases will in turn decrease despite the lower demand exerted, because the rate of reaeration decreases with increasing dissolved oxygen levels until ultimately the dissolved oxygen reaches the saturation value again and the stream reaches a condition of equilibrium. Since the rate at which deoxygenation takes place is more or less constant, the controlling factor in the length of time required to complete the cycle of oxygen sag curve and reach an equilibrium depends primarily upon the reaeration characteristics of the stream, temperature, and quantity of pollution. In other words, two streams receiving the same amount of pollution may complete the cycle of self-purification at different times depending upon the physiographic and hydrological condition of the stream under otherwise identical temperature conditions. There is some evidence that the rate of deoxygenation may be influenced by stream characteristics and that it may be more rapid in shallow, turbulent streams than in deep sluggish ones, in spite of the fact that the opportunity for removal of BOD by sedimentation in turbulent streams is lower. Better cover in the form of submerged plants in pools and stones covered with biological growths apparently increases the removal by adsorption and oxidation.

The course of events described above on the basis of normal accepted rates of deoxygenation is presented graphically in Figure 1. It is also formulated as follows:

$$D = \frac{k_1 La}{k_2 - k_1} (10^{-k_2 t}) - (10^{-k_1 t}) + Da 10^{-k_2 t}$$

in which La is the initial BOD and Da the initial oxygen saturation deficit; k_1 is the deoxygenation coefficient and k_2 the reaeration coefficient; D the saturation deficit after t days. With Da , La and the two constants known, the deficit may be calculated for any point downstream. The equation may also be solved to determine the reaeration constant k_2 .

This course of events is predicated on the basis of a massive source of

pollution at one point with no further pollution or dilution at intervening points, which is an idealized picture seldom realized.

Modifications introduced by tributaries and additional pollution only complicate the picture but do not change the general course of events. Other modifying factors, such as temperature, influence the oxygen sag curve through the simultaneous effect on deoxygenation and reaeration rates.

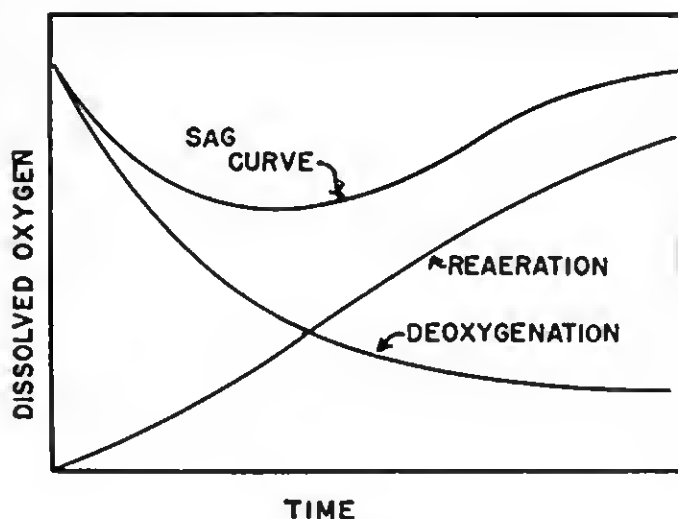


FIGURE 1

Effect of Industrial Wastes on Self-purification

The effect of industrial wastes on the biochemical activities associated with self-purification may be the same as that discussed for sewage or may differ materially. White water from the paper industry compares favorably in physical characteristics and strength to domestic sewage. It consists primarily of suspended, colloidal and dissolved organic matter. However, it contains more fiber and less nitrogenous matter than sewage and naturally no pathogenic organisms. The discharge of such a waste would therefore have the same general effects as sewage. Cannery and slaughterhouse wastes have characteristics similar to sewage, except for differences in strength. Another group of wastes contains only materials in true solution or in finely dispersed state such as dairy, citrus fruit, brewery, alcohol fermentation, yeast production, penicillin production, certain solvents, and sulfite liquor wastes. Such wastes will not cause sludge deposits except for secondary sludge which arises from the biological growths produced from the oxidation of the pollutional materials. Extensive biological growths produced as a result of discharge of such wastes ultimately slough off and may form sludge deposits. Only under

exceptional cases is the accumulation from this source sufficient to cause a real problem. The main problem associated with the discharge of such wastes is the heavy oxygen demand exerted in the flowing portion of the stream. Many of these wastes are much stronger than domestic sewage. The deoxygenation rate (k_1) of wastes is assumed to be the same as that for sewage but it is conceivable that some wastes may have higher rates due to greater availability of soluble organic materials. Certain reduced compounds such as sulfur dioxide associated with sulfite liquor waste may exert initial deoxygenation rates much higher than the biochemical rates established for sewage because of the possibility of chemical oxidation.

Another group of wastes further removed from sewage by its effect on biochemical deoxygenation includes those which contain, in addition to oxidizable organic materials, either organic or inorganic toxic substances. Examples of this group are petroleum refining wastes, gas house wastes and certain types of chemical wastes. It is difficult to predict the effect of such wastes on the self-purification mechanism of the stream without knowing the nature and concentration of the inhibiting agents and the organic oxidizable materials, as well as the degree of dilution in the stream. The normal deoxygenation constants of sewage may not apply for such wastes unless the dilution is sufficiently high to overcome the influence of the inhibiting agents. The effect otherwise will be one of arresting temporarily the deoxygenation and preserving a high level of dissolved oxygen in the presence of oxidizable material. With additional dilution further downstream, or by deactivation of the inhibiting agent by physical, chemical or biological agencies, the biochemical oxidation eventually starts to exact its toll on dissolved oxygen further downstream, rendering the intervening zone biologically barren. It is important in this connection to differentiate between the inhibiting effect of organic and inorganic poisons. Organic inhibiting agents such as phenols may retard the oxidation of other nontoxic organic materials at a given concentration, but at a lower concentration the oxidation of other organic compounds will proceed and the phenol itself will exert an oxygen demand. Inorganic poisons, on the other hand, can only prevent the oxidation of organic materials and normally will not exert an oxygen demand of their own, except when they are in a reduced state.

There are finally purely inorganic wastes such as acids, alkalies, cyanides, plating liquor wastes, etc. These are not objectionable because of their oxygen-consuming properties, but because of their harmful effect on the mechanism of self-purification and biological population of the stream.

Biochemically inactive wastes such as culm, sawdust or clay are not

objectionable because of their deoxygenating effect, but because of the destruction of fish breeding and feeding grounds as a result of their deposition.

Sludge Deposits

Sludge deposits are formed by the deposition of settleable solids discharged in sewage and wastes, augmented by flocculated finely divided materials in the stream and secondary sludge. Most of the solids are deposited near outlets where the velocity in the stream becomes insufficient to keep them in motion. Decreasing quantities are spread over wider stretches. The deposits are not static. During freshets and high flows they may be lifted and carried some distance before they are redeposited in sluggish coves.

Organic deposits are generally mixed with clay and silt and usually have a lower volatile matter content than suspended organic materials. There is a tendency for compaction and consolidation with time. Anaerobic conditions prevail throughout the depths except at the extreme surface of the deposit in contact with the oxygenated flowing water. As a result of physical consolidation, gas evolution, and the movement of burrowing animals such as worms, etc., which abound in such an environment, a strict separation between the anaerobic and aerobic zones is not obtained. Instead, some of the solid particles are brought from the lower levels to the surface. Soluble and colloidal products of anaerobic digestion either diffuse or are brought to the surface of the deposit by various forces. The over-all biological reaction in the bottom deposits, including the anaerobic and aerobic phases, is referred to as benthic decomposition. The oxygen demand exerted by the thin aerobic zone is of the same order and rate as an equal amount of the material kept in suspension in the flowing portion of the water, except that it is augmented by the materials coming to the aerobic zone from the lower sections of the deposit. In other words, if all the deposits were spread in a very thin layer on the river bed so that the sludge was stabilized by purely aerobic processes, the oxygen demand exerted would be equivalent to the same material kept in suspension. The anaerobic decomposition in the lower sections does not exert an oxygen demand except by diffusion and transport of soluble and colloidal material to the aerobic zone. Under conditions of active fermentation the deposits may float to the surface of the stream and after releasing entrained gas may sink to the bottom again. Additional oxygen from the stream itself may be utilized by this method of gas lifting of sludge and consequent elutriation of the products of anaerobic decomposition into the flowing portion of the water. Transportation of sludge deposits during flood flows has a similar effect except that during this period the demand exerted will

be negligible in relation to the supply of oxygen available in the stream water. With these exceptions, anaerobic decomposition of sludge deposits may be considered of benefit to the oxygen economy of the stream to the extent that the organic matter is converted to methane and hydrogen, which escape to the atmosphere without being oxidized to carbon dioxide and water.

As the depth of the deposits increases from a thin aerobic carpet to a thicker layer the proportion of the organic matter stabilized anaerobically increases, exerting a beneficial influence on the oxygen economy of the stream as a whole. However, since the same amount of organic matter is concentrated in a smaller area the over-all localized effect will be worse, since the total oxygen demand per unit area will increase.

Bacterial Self-Purification

It was stated previously that two general types of bacteria may be differentiated in a stream; namely, the native water population and the pollutional forms, such as the coliform organisms. In the biochemical oxidation of the pollution, the coliform organisms play only a minor role. The native water forms are most active in this respect. It is to be expected that the numbers of water forms increase as a result of pollution and during the period when active biochemical oxidation is taking place. With the decrease in the quantity of oxidizable materials and the reduction of biochemical activity, their numbers decrease. The changes in the numbers of native bacterial population cannot be readily demonstrated since most of them cannot be grown on the usual culture media used. What passes for a total bacterial count includes only the pollutional forms and some of the more readily cultivated organisms of the nonpollutional type. Observations on the numbers of bacteria in a polluted stream either by plate counts or of the coliform organisms, therefore, indicate the same general trend. A number of investigations have shown that bacteria and coliform organisms increase slightly below a sewer outlet. The exact cause for this increase is not understood, although it has been ascribed to possible multiplication or dispersion of bacterial aggregates. The numbers thereafter decrease regularly until a minimum level is reached. The decrease in bacterial numbers parallels roughly the decrease of organic materials by biochemical oxidation. Attempts to predict the changes in bacterial numbers in streams from laboratory studies are not as quantitatively applicable as in the case of deoxygenation. The initial rise of bacteria in the bottles is higher and the decrease is slower than in the stream itself. Otherwise the same general trends prevail.

The forces that affect decrease of bacterial numbers in the streams are:

(1) *Sedimentation*. Although bacteria settle at a slow rate because of

their small size, they are usually found in aggregates or attached to larger particles which upon settling remove a considerable number of bacteria.

(2) *Protozoa*. Many of the ciliated protozoa ingest large numbers of bacteria as well as particulate matters. Such an action contributes to a significant decrease in bacterial numbers in the stream since bacteria-feeding protozoa are found in considerable numbers.

(3) *Food Supply*. Food supply even in a polluted stream cannot be considered as abundant as judged by bacteriological standards of culture medium. Furthermore, the nature of the organic matter is such that it does not favor the growth of pollution organisms. Coliform organisms will grow in dextrose peptone medium, but a stream polluted by sewage or most industrial wastes does not contain a sufficient concentration of such readily available organic materials as dextrose and peptone. Coliform

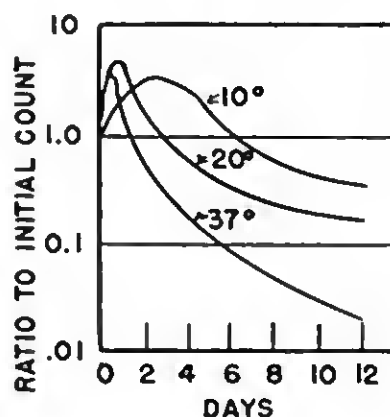


FIGURE 2

organisms inoculated into sterile sewage will not multiply or transform organic materials. The biochemical oxidation of organic matter in a stream further reduces the limited supply of food.

(4) *Temperature*. The temperature of the stream water even during the summer is below the optimum for the pollutional bacteria. In general, the effect of higher temperature is to stimulate the growth of bacteria in the presence of abundant food supply and favorable environmental conditions. When the food supply is limited, and conditions are not favorable for growth, the effect of increasing the temperature within the growth range is to cause a more rapid death rate. The decrease of bacterial numbers during summer is higher than during winter (Figure 2).

(5) *Sunlight*. Sunlight has bactericidal properties but the role played under actual stream conditions in decreasing the numbers of bacteria is probably insignificant because of the poor penetration of the ultraviolet rays to any great depths even in clear water. In turbid waters the penetration is greatly reduced.

(6) *Bacteriophage*. The destruction of bacteria can take place under favorable conditions by the lytic action of virus-like bacteriophage which is parasitic on bacteria. However, the importance of bacteriophage in reducing the numbers of bacteria in streams is questionable because the action is dependent upon a delicate adjustment of environmental conditions. Bacterial lysis occurs only under conditions which favor a rapid multiplication of bacteria. This condition does not occur in the stream as far as the intestinal group of bacteria is concerned.

(7) *Industrial Wastes*. Industrial wastes seldom contribute appreciable numbers of polluttional bacteria to the stream. The discharge of organic non-toxic wastes can result in an initial increase in bacterial numbers in a stream, followed by a decrease as the food becomes exhausted by biochemical oxidation. If the discharged wastes have toxic materials the effect will be an immediate and sharp decrease of bacterial numbers.

BIOLOGICAL ZONES IN A POLLUTED STREAM

The over-all physical, chemical and biological changes brought about as a result of discharge of sewage and other oxidizable organic wastes have been divided into different zones on the basis of various criteria. Brinley¹ proposed a system of zoning on the basis of biological characteristics as follows:

Zone I. Zone of Active Bacterial Decomposition. This zone is immediately below the source of pollution and is characterized by a low dissolved oxygen content (between 3 to 0 ppm), a high BOD, a high bacterial count, the presence of bacteria-eating protozoa such as *Paramecium*, *Colpidium*, *Vorticella* and *Carechesium*, and a few flagellates. The total volume of plankton is low. In the bottom deposits are found *Tubifex* and *Limnodrilus* worms. Gas evolution often brings sludge to the surface. Sewage fungus is present. Only a few coarse fish such as carp and buffalo are found at the mouth of the sewer.

Zone II. Zone of Intermediate Bacterial Decomposition. The rate of biochemical activity is decreased and as a result the dissolved oxygen increases to 3 to 5 ppm. The plankton volume is higher but the plankton is still made up of polluttional forms requiring a rich medium or feeding on bacteria and solid particles. There is an increase in green and blue-green organisms. In addition to carp and buffalo, shiners, minnows, suckers and sunfish are found.

Zone III. Fertile Zone. This zone has a dissolved oxygen content above 5 ppm and is characterized by a large variety and volume of green algae and a decrease of polluttional protozoa. The fertilizing effect of the decomposed sewage and wastes has resulted in an increase in biological productivity. Forage and market fish increase in numbers.

Zone IV. Game Fish Zone. In this section the plankton volume diminishes sharply and only the clean water forms remain. The dissolved oxygen level remains near the saturation point. Bass, perch, wall-eyed pike and other game and forage fish predominate.

Zone V. Biological Poor Zone. Plankton volume is even lower in this zone and consists entirely of clean water forms. Fish are scarce in comparison with the previous zone and are mainly forage and game fish. The reduction of fish is associated with the low plankton population resulting from the exhaustion of available food.

EFFECT OF WASTES ON FISH LIFE

It does not follow that the indiscriminate discharge of sewage and wastes is desirable from the standpoint of fertilization for biological growth and fish. Excessive amounts of sewage and waste will, on the contrary, have deleterious effects on fish life.

According to Ellis,² the injurious effects of industrial wastes and sewage are caused by the following factors:

(1) Materials in suspension such as in untreated sewage, paper pulp, mud, sawdust, rock powder, etc., cover the bottom and smother the biological life therein which is important as fish food.

(2) Materials having an oxygen demand reduce the dissolved oxygen content of the stream to a point where fish cannot exist. It is not the organic matter *per se* that kills the fish, but the low dissolved oxygen content resulting from the biochemical activities. A dissolved oxygen content of 5.0 ppm is taken as the minimum for game fish, but the value is affected by various other factors.

(3) Acid or alkaline conditions created in the stream by the discharge of waste affect the fish life directly. Most fish require a pH value of 6.5 to 8.4. Wastes derived from chemical and plating works and coal mines seriously affect fish life.

(4) Salinity of the water is important for fresh-water fish as they cannot tolerate sudden changes in osmotic pressure. Brines from oil wells are detrimental in this respect; about 7,000 ppm of NaCl is usually lethal to fresh water fishes.

(5) Fish are killed specifically by toxic substances even when all other conditions of the environment are favorable. Most of these toxic materials are effective in very low concentrations. The effects may be cumulative or indirect by the destruction of their food supply.

(6) High CO₂ concentration in water is also inimical to fish.

Sensitivity to specific pollutants varies with the species, age, weight of fish and seasonal effects. Fish are most sensitive just after the breeding season, and within a given species the smaller fish are more resistant than

larger or adult ones. Trout is most sensitive and goldfish, carp and bullheads are most resistant.

The unfavorable results of polluting materials may be divided into indirect and direct effects. Indirect effects are created by the destruction of the food supply by covering the river bed by inert or oxidizable matters or by the destruction of spawning beds. Materials in suspension also decrease light penetration and limit the green plants which serve as a part of their food supply.

Low oxygen levels are more fatal at higher temperature than at lower temperatures. A combination of high CO_2 and low dissolved oxygen content which normally occur at high temperatures is particularly deleterious.

Direct acting pollutants create a lethal effect either through (a) their action on the epithelial surfaces of the gills, or (b) by absorption through the body affecting the internal structure and metabolism of the fish.

Oil wastes, acids and salts or heavy metals and phenols may produce their lethal effect by acting upon the mucous of the gills by clogging and coagulating them.

In the second type of toxic pollutants which act by absorption into the body are acids, phenolic wastes, ammonium compounds such as derived decomposition products of organic matter and gas house wastes, sulfur compounds such as hydrogen sulfide and methyl mercaptans, cyanides, arsenic, chlorine, etc.

In the case of acids and phenolic wastes, which act both by coagulating the mucous on the gills and by direct absorption, the gills are affected first.

Various ions may combine to increase the toxic effects or may decrease them.

The topography and soil formation also play an important role in fish life. Hilly country, bare of vegetation, is conducive to erosion and the resultant silt upon deposition covers the breeding and feeding areas of fish. Too high a grade in the stream is not conducive for the growth of algae and aquatic plants and thus deprives fish of food and shelter.

References

1. Brinley, Floyd J., Biological Studies, Ohio River Pollution Survey I. "Biological Zones in a Polluted Stream," *Sewage Works J.*, **14**, 147-152 (1942).
2. Ellis, M. M., "Industrial Wastes and Fish Life," *Proc. 1st Ind. Waste Util. Conf.*, Purdue University, 126-134 (1944).
3. Kittrell, F. W., and Kochtitzky, O. W., Jr., "Natural Purification Characteristics of a Shallow Turbulent Stream," *Sewage Works J.*, **19**, 1032-1047 (1947).
4. "Standard Methods for the Examination of Water and Sewage," 8th Ed., New York, Am. Pub. Health Assoc. (1936).
5. Streeter, H. W., "Standards of Raw and Treated Water Quality," *J. Am. Water Works Assoc.*, **31**, 1479-1488 (1939).

3. Milk Products Waste

E. F. Eldridge

*Washington State Pollution Control Commission
Olympia, Wash.*

THE MANUFACTURING PROCESSES

The milk industry is one of the most widely spread of all industries. Almost every city or village regardless of location has one or more plants

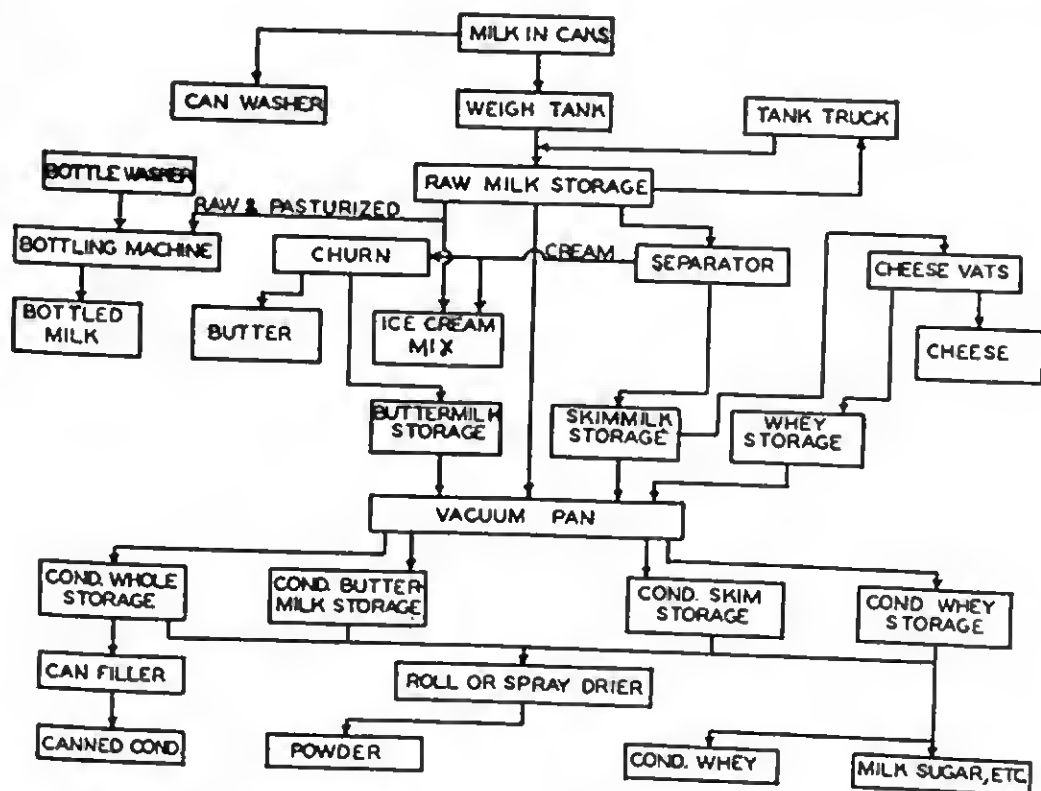


FIGURE 1. Composite flow diagram of milk products operations

in which milk products are processed. These vary from small receiving stations to large plants where most of the products made from milk are manufactured. Figure 1 is a composite flow diagram showing the major operations for the processing of the more common milk products. Few

plants are equipped for all of the operations shown, but may employ any one or a combination of several. The following is a brief description of these processes.

Milk is received at the plant or receiving station in standard 80-lb cans. It is dumped to a weigh vat and the cans are washed in a can washer and returned to the producer. From the weigh vat the milk is pumped to a storage tank or, if the plant is a receiving station, the milk is cooled and pumped to a tank truck for hauling to a bottling or processing plant.

About 50 per cent of the milk produced in this country is used as whole milk.⁹ A small amount of this is bottled as raw milk, but the major portion is pasteurized prior to further handling. Pasteurization is accomplished by heating either to 143°F for 30 minutes or to 160°F for 15 seconds. The milk may then be bottled for distribution, condensed to produce evaporated milk, or dried to a milk powder. A small amount of whole milk is used in the manufacture of ice cream mixes and in some types of cheese.

About 41 per cent of the milk supply is separated into cream and skim milk. Some of the cream is bottled for distribution or is used for ice cream mix. A considerable portion, however, is used in the manufacture of butter. In some cases the producer may separate the cream and deliver it to the plant where it is cooled and processed. Buttermilk is a by-product of butter manufacture and may be condensed in the vacuum pan or may be dried on heated rolls with or without precondensing. Powdered buttermilk is used mainly in the preparation of stock and poultry feed.

Skim milk from the separator may be condensed in the vacuum pan and/or dried to produce skim milk powder. Condensed and powdered skim are used in food products and animal feeds. Some of the skim milk may be used for the manufacture of cottage cheese and casein.

Whey is a by-product of cheese manufacture and is used in small plants for hog feeding. If the operations are large enough to warrant, it may be condensed in the vacuum pan or dried in a spray drier. Condensed and powdered whey are also used in food products and in animal feeds. In a comparatively few plants condensed whey is used for the manufacture of milk sugar, lactalbumin, lactic acid, alcohol or vinegar.

SOURCES OF WASTE

Wastes from milk products manufacture contain milk solids in a more or less dilute condition, but in varying concentration. These solids enter the wastes from almost all of the operations. In general the wastes and their sources may be classified as follows:

- (1) Spoiled raw or manufactured products.
- (2) By-products (buttermilk, skim milk and whey).

- (3) Spillage or overflow due to inefficient equipment and careless operations.
- (4) Rinsings and washings from cans, equipment, and floors.
- (5) Condenser water and condensate from vacuum pans.
- (6) Water from coolers, ice machine, boilers and roof drains.

BOD OF WHOLE MILK AND BY-PRODUCTS

Milk solids are composed of the three general classifications of organic material, namely, fats, proteins and carbohydrates. Roughly, the BOD of one pound of milk fat is 0.89 pound. One pound of milk proteins is 1.03 pounds, and one pound of milk sugar is 0.69 pound. The milk solids content of whole milk and hence that of skim milk, buttermilk and whey varies to some extent. The average compositions of these products are given in Table 1. Since milk wastes are made up of dilutions of whole milk and the by-products it is of value to know the range of BOD concentrations of these products. The following data have been obtained from the analysis of a large number of samples⁴:

TABLE 1. AVERAGE CONTENT OF MILK AND BY-PRODUCTS (LBS PER 100 LBS)

	Protein	Fat	Lactose	Total Solids	Organic Solids	BOD
Whole milk	3.2	3.9	5.1	12.9	12.2	10.3
Skim milk	3.3	0.1	5.3	9.5	8.7	7.2
Buttermilk	3.4	0.4	4.3	9.4	8.7	7.2
Whey	0.9	0.3	4.9	6.9	6.3	3.5

5-day BOD, ppm	
Whole milk	90,000 to 105,000
Skim milk	65,000 to 75,000
Buttermilk	55,000 to 65,000
Whey	25,000 to 35,000

Roughly, 100 pounds of whole milk will have about 10 pounds BOD and a population equivalent of about 60.

WASTE PREVENTION

Waste disposal in the milk industry may be divided into two programs, first, waste prevention or saving, and second, waste treatment. The utilization of by-products and a waste-saving program will materially reduce the loss of milk solids and simplify the requirements for treatment.^{1,10,11} Such a program should always precede the design of treatment facilities.

The first step in the program is to segregate all possible clean water from the water containing milk solids. Segregation necessitates changes in the drain system of the plant in order to provide a separate line for cooling water, ice machine water, boiler blow-down, roof drains and

vacuum pan water. The condenser water from the vacuum pan will contain entrained solids and will be discussed later, but because of its large volume it must be segregated from the plant wastes.

After as much of the clean water has been segregated as can be economically accomplished, a weir box containing a device for measuring the rate of flow and an automatic sampler is installed on the waste line. The laboratory is then provided with facilities and instructed in the pro-

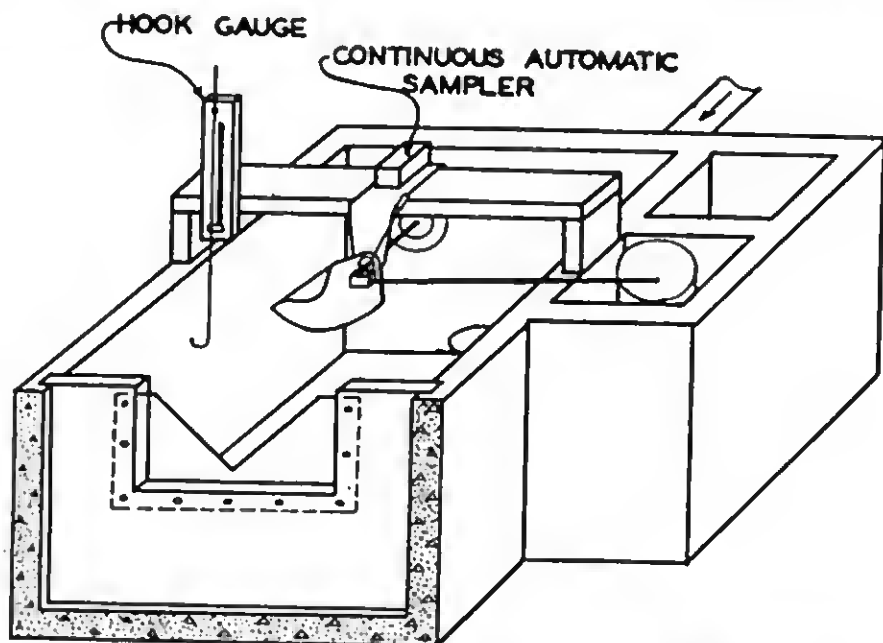


FIGURE 2. Continuous automatic sampler and hook gauge installed in a 90° V-notch weir box

cedure for the BOD test. Figure 2 shows a weir box with a 90° V-notch weir, hook gage, and Trebler automatic sampler. A regular program of sampling and analysis is initiated before any waste prevention activities are started and is continued until losses are reduced to a minimum. After this point has been reached occasional measurements and analyses are necessary to prevent a return to careless operations.

The prevention program consists of a study of the various sources of waste, and the initiation of good housekeeping methods, careful operations, by-product utilization, employee education, and adequate and efficient facilities. Some of these activities are discussed in the pages which follow.

DISPOSAL OF SPOILED PRODUCTS

Spoiling usually occurs during periods of hot weather when cooling facilities may prove to be inadequate. More attention has been given in recent years to the handling of milk by the producer and spoilage is not as great as it was at one time. Spoiling may occur in the plant due to

prolonged power failure, breakdown of equipment, or lack of adequate storage.

It is a general rule that spoiled products are not to be dumped into the drain system, except perhaps in very large cities where the quantity of sewage is so large that the spoiled material will have no apparent significance. Provision should be made to prevent spoiling by installing adequate equipment and emergency power. When products do spoil, they should be returned to the producer for feeding purposes.

UTILIZATION OF BY-PRODUCTS

It should be a general rule in all plants where milk is processed that by-products should not be allowed to enter the drain systems. The quantity of these by-products is not always amenable to processing for use as food products or animal feed. In these cases adequate provision must be made to return the entire amount of by-product which cannot be sold as such to the farms for feeding purposes.

Where the volume is sufficiently large to warrant processing, adequate provision must be made to take care of the by-product at peak season. In some cases, it may be feasible for several plants to combine for processing by-products, if the length of haul is not excessive. There are numerous plants designed especially for by-product processing which take the material from a fairly wide area.

In general, these processes consist of removing the water and recovering the solids in a semi-solid or dry condition.

Skim Milk and Buttermilk

Considerable quantities of skim milk are processed for the manufacture of both plain and sweetened condensed skim and for dry powder. Single- or double-effect evaporators are used for condensing. Dry powder is produced by either spray or roll drying. A good share of these products go into the manufacture of food.¹

Buttermilk is also condensed or powdered. The concentrate is used extensively in feed for animals. Since buttermilk has a much higher solids content than whey, economical processing is possible with smaller volumes, although it is usually an advantage to haul to a central condensing plant if the creameries are suitably located.

Dry powder is usually produced by roll drying the buttermilk directly or after precondensing. It may be spray dried in certain types of driers. As much of the butter washings as possible should be included with the buttermilk in processing. The first rinse should therefore be of as small a volume as possible and should be collected. Where condensing or drying facilities are not available, the buttermilk and first washing should be collected and

used for feeding in the fluid form. There is a limited market for fluid buttermilk for human consumption.

Cheese and Casein Whey

Whey is the most dilute of the by-products and for this reason larger volumes are necessary to make processing economical. William A. Dean in a report of the dairy Task Committee¹ indicates that 100,000 pounds of whey per day should be available during the flush season to economically operate a double-effect evaporator, and 250,000 pounds of fluid whey for the operation of a spray drier. Most of the whey powder produced is made by precondensing in single- or double-effect evaporators and then spraying to form the powder. This means that the condensing plant must serve several cheese factories and that the drying plant must take the condensate from several condensing plants. It is estimated that the economical haul for fluid whey is up to 40 miles and up to 150 miles for concentrate.

Roll drying can be used for fluid whey and has the advantage of lower equipment cost. Economical operation of a roll is possible with as low as 30,000 pounds of fluid whey per day. The principal use for powdered whey is in the manufacture of poultry and animal feeds. A relatively smaller amount is mixed with other materials for food products.

In addition to whey powder, a number of other products are produced from whey, such as milk sugar, lactalbumin, lactic acid, alcohol, vinegar, and sweetened condensed whey. The manufacture of all of these, except whey concentrate, is accompanied by a waste disposal problem which, mainly because of the comparatively high concentration of solids is of greater intensity and sometimes more difficult than most other milk waste problems. The manufacture of whey concentrate and powder adds to the waste problem because of losses during operation and clean up, but the production of products such as milk sugar, etc., results in a residue which is very concentrated and for which the market is limited. These residues can be dried in the same manner as whey concentrate.

Both sweet and sour whey concentrate are manufactured. Because of the high acid content the sour concentrate is not nearly as perishable as the sweet, however, it is very corrosive to pans and equipment. The investment in equipment for the manufacture of the concentrate is smaller than for whey powder, but the difficulties and cost of transportation are greater.

SPILLAGE AND OVERFLOW

Spillage and overflow of milk and milk products are caused by inadequate equipment and careless operations. Following are some of the more common methods and facilities used to prevent these losses:

(1) Electronic liquid level controls and alarms are used on storage tanks, vats, upper and lower cooler troughs and other receptacles where there is danger of an overflow of milk or other products.

(2) Temperature controls are installed on coolers to prevent the milk from freezing on the plates.

(3) Temperature regulators are used to prevent hot-wells from boiling over.

(4) Where possible, stand-by electric power is provided to avoid the necessity of dumping milk and by-products when the usual source of power fails.

(5) Adequate storage tanks and processing equipment are necessary for handling the peak volume of milk to avoid waste and spoilage.

(6) Preventive maintenance of equipment and piping and replacement of worn-out or old style parts prevents or corrects leakage.

(7) Foaming is prevented by avoiding air leaks in pump suction lines, pump packing or rotary seals.

(8) Modern style separators are installed to avoid the loss of solids which occurs by foam from older types.

(9) Cheese vats are not filled above 3 inches from the top to prevent spillage.

(10) Storage tanks with a capacity of one and one-half the maximum daily volume are necessary in order to make adequate disposition of whey.

(11) Entrainment separators on vacuum pans are strongly recommended to minimize the carry over of milk solids in the condenser water.

(12) In cases where the pollution problem is extremely acute, surface condensers are installed on vacuum pans to collect the condensate for treatment.

(13) Electronic water level controls are used to operate an alarm and to break the vacuum on pans to prevent them from boiling over.

(14) A stand-by pump installed to pump whey from the cheese vats to storage will avoid the discharge of whey to the drains.

RINSINGS AND WASHINGS

The only unavoidable wastes from a milk products plant are those resulting from rinsing and washing tanks, cans, equipment, and floors. Considerable waste can be prevented here by careful operations and the installation of adequate waste-saving facilities. The following list includes some of the more common methods used to control these wastes:

(1) Much of the milk which remains in the can after the milk is dumped to the weigh vat can be collected by installing a drip saver and prerinse on the can washer. Very little water is required for the prerinse (about 3 ounces per can). However, it should be injected into the cans in

the form of a fine spray. The drip and rinse are collected in a special can or tank and used in the product, if possible, or for animal feeding.

TABLE 2. BASIC DATA FOR CALCULATING STANDARD MAXIMUM LOAD

Process	Lbs BOD per 10,000 lbs milk or equivalent for 1st 50,000 lbs handled	For each 10,000 lbs over 50,000 lbs intake
Receiving and cooling milk	7	6
Tank truck delivery to and from plant	1	1
Storage in tanks	1	1
Evaporating whole milk, floor waste	4	3
Evaporating whole milk, entrainment loss	2	2
Canning and sterilizing evaporated milk	4	3
Spray drying	4	2
Cream separating	4	4
Cream pasteurization, cooling and can filling	4	4
Cottage cheese or casein	16	16
American cheese, unwashed curd	10	8
American cheese, washed curd	16	14
Skim condensing, plain, floor waste	6	6
Skim condensing, plain, entrainment loss	3	3
Skim condensing, sweetened, floor waste	8	8
Skim condensing, sweetened, entrainment loss	3	3
Skim condensing, superheated	12	12
Skim drying, spray	4	2
Skim drying, roll	20	10
Whey condensing, sweet, floor waste	16	8
Whey condensing, sweet, entrainment loss	4	4
Whey condensing, acid, floor waste	12	8
Whey condensing, acid, entrainment loss	3	3
Whey drying	10	6
Buttermilk condensing	12	8
Milk pasteurization, cooling and bottling	10	8
Ice cream mix, vat	8	6
Ice cream mix, pan	8	6
Ice cream freezing	2	2
Cultured buttermilk making	10	10
Butter churning and washing	6	6

(2) The use of a constantly discharging water hose in the receiving room or other rooms increases the volume of waste to be treated and should be avoided.

(3) Pipelines used to transport milk or milk products are installed in such a manner that they can be easily drained into standard buckets before they are disassembled for washing.

(4) Tanks and vats are drained thoroughly and the milk or product collected.

(5) Cheese vats are directly connected to the whey pump suction line to avoid spillage of whey. Cheese washings, especially the first and more concentrated, are added to the whey for processing or feeding purposes.

(6) The first butter washings are collected and processed with the buttermilk.

"STANDARD MAXIMUM LOAD"

H. A. Trebler of National Dairy Research Laboratories, in an unpublished report, has prepared from experience in a large number of milk products plants a method for the calculation of, what he has called, the "standard maximum load." This is the average BOD load for "the 10 consecutive days during the year which give the highest average daily milk volume processed, assuming that the plant has good management and personnel and adequate modern equipment to handle its maximum volume and that every effort is made to follow good housekeeping and normal waste saving practices." This calculated value gives the plant management something to strive for in a waste prevention program, although it cannot be expected that every plant will meet the value. Some may arrive at a value considerably less than the calculated one, while others will find it impossible to reach at all. Table 2 has been prepared by Trebler for calculating the standard maximum load for any given plant. This table gives the lbs of BOD for each 10,000 lbs of milk handled in the various process steps.

The following example is given by Trebler to demonstrate the calculation of the standard load from the values in Table 2. An evaporated whole milk plant receives an average of 80,000 lbs of milk during 10 top days. Of this, 60,000 lbs are received direct from the producer in cans, and 20,000 lbs comes in tank trucks. The standard load is calculated as follows:

Receiving in cans (5 x 7) + (1 x 6)	41
Receiving by truck 2 x 1	2
Storage in tanks 8 x 1	8
Evaporating whole milk (5 x 4) + (3 x 3)	29
Canning and sterilizing (5 x 4) + (3 x 3)	29
	<hr/>
Standard load, lbs BOD per day	109

In addition the normal entrainment loss in the pan water will be 16 lbs per day.

TREATMENT OF MILK WASTE

The wastes from the processing of milk products are almost entirely composed of organic material in solution, or colloidal suspension, although some larger suspended organic solids may be present in such wastes as

those from cheese and casein operations. Sand and other foreign particles will be present in limited amounts as a result of cleaning up the floors.

If these wastes are held for a short time, fermentation of the milk sugar will produce lactic acid and cause precipitation of the casein and other protein material. If stored in a condition which allows anaerobic action the waste rapidly becomes septic and odorous. Milk solids, especially the carbohydrate material, are readily oxidized biologically under aerobic conditions.

Treatment Processes

Since milk waste contains very little suspended matter, preliminary settling for solids removal does not result in an appreciable reduction of the BOD. In most cases the amount of sand and other floating material in the waste is sufficient to warrant a small screen and grit removal chamber. The structure for this purpose will be discussed later.

Aerobic processes are best adapted to the treatment of milk waste. The selection of the process for any particular plant will depend upon the size of the problem, location of the plant, and the necessary degree of treatment. The following processes are recommended:

Land irrigation
Aeration

Biological filtration
Activated sludge

In some cases it has been considered desirable to treat the concentrated by-products, such as whey or "mother-liquor" from milk sugar manufacture, rather than to utilize them in the manufacture of feeds or other products. This is not an economical practice, but if it is considered desirable for any reason, these by-products can be successfully treated by the anaerobic digestion process. In many cases it will be necessary to provide aerobic treatment for the effluent from the digestion process in order to reduce the BOD to the desired level. Each of the above aerobic processes is discussed in some detail in the following portions of this chapter.

Land Irrigation

Surface irrigation may be used as a means of waste disposal by small plants located on farms or in sparsely populated areas. This method can be used only during the summer months in temperate zones, but has a much wider application in warm and arid regions.

The land to which the waste is applied must be kept under constant cultivation in order to prevent pooling and the production of odors. The land may be furrowed and crops planted between the furrows. The soil must be light and sandy and may be underdrained with parallel rows of

farm tile located about 15 inches below the surface. Drainage is not necessary, but aids in removing the excess water from the soil and increases the capacity for handling the waste. The waste may flow by gravity or be pumped to the field depending upon the topography of the area, but in either case provision should be made to apply the waste to alternate portions of the field in order that each area can be allowed to dry and can be cultivated between applications.

If odors become a factor in the use of this method of disposal they may be controlled by the application of liquid chlorine or sodium hypochlorite to the waste before it is applied to the field. E. A. Reinke⁸ has found that a dose of 20 ppm chlorine is sufficient to control odors.

Screen and Grit Chambers

Screening to remove large particles such as matches and milk bottle caps prevents much of the trouble with clogging of pumps and other equipment. A screen of $\frac{1}{2}$ -inch mesh wire is installed in a chamber in the drain line, if the line is not too deep. It is built on a frame which can be removed for cleaning.

The screen chamber can also be used for the removal of grit by building it of a size which will reduce the average velocity of flow to about 1 foot per second. This velocity is sufficient to keep most of the organic solids in suspension while allowing the sand particles to settle. The chamber requires frequent cleaning and a closed container should be available to hold the grit and screening until they can be disposed of by burying. This screen and grit chamber should precede all types of treatment except perhaps those for very small plants.

Aeration and Preaeration

The operations of a milk plant are not uniform and the flow and concentration of the waste will vary over a wide range. There are periods of great activity in the plant when the waste may be very strong. This condition may also prevail during the final wash-up period. At other times, especially at night, the waste may consist entirely of clean water. Because of this wide variation of the waste, and since it is desirable to operate treatment facilities at a more uniform rate over as much of the entire day as possible, provision is made for storage and equalization.

Air is applied to the waste in the equalizing tank to avoid the production of odors and septic conditions. It has been found that this application of air, if extended over a period of 18 to 20 hours, results in a reduction of the BOD varying from 30 to 60 per cent and averaging about 45 per cent. Also, during this aeration and storage period much of the milk sugar (lactose) is converted to lactic acid by the action of fermenting organisms.

In this condition it is more readily oxidized on the biological filter or by activated sludge.

A period of aeration is, therefore, desirable either as a means of treatment in itself or preliminary to other aerobic processes and for the equali-

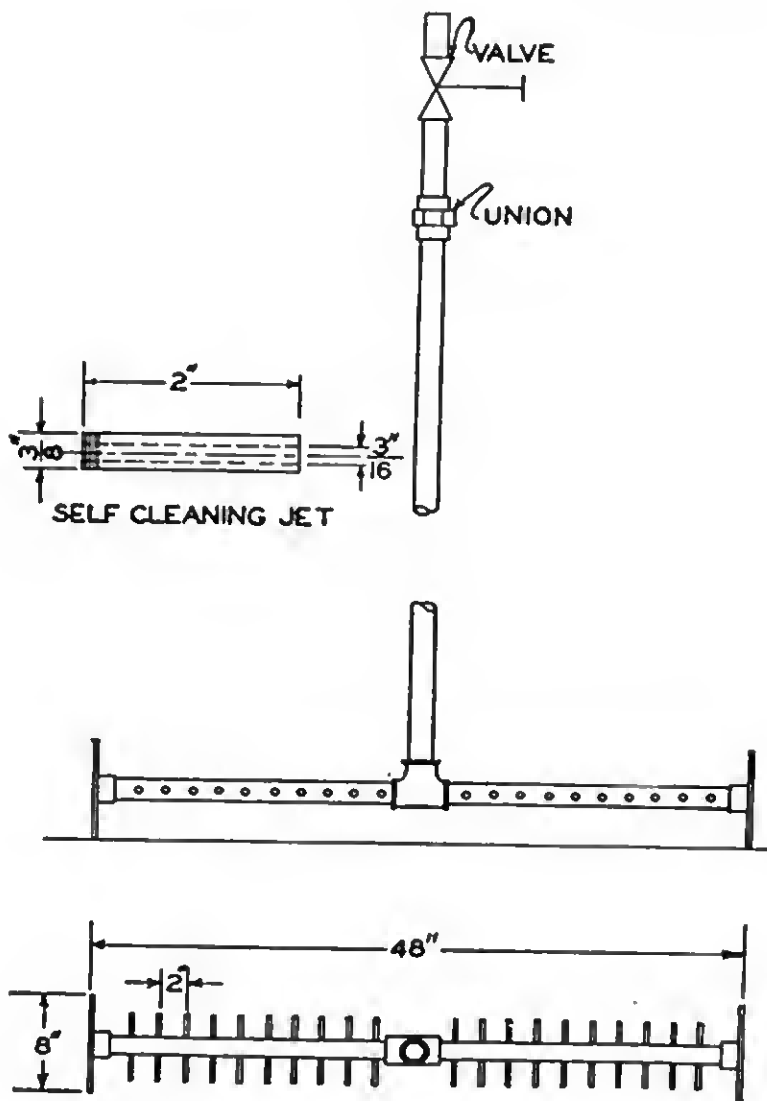


FIGURE 3. Self-cleaning jet diffusers for aeration of milk waste

zation of flow and concentration. In some cases the reduction obtained from simple aeration of this type may meet the requirements for treatment of the waste. This is especially true if the waste is to be discharged to the sewerage system of a municipality.

The process will gradually develop a sludge which materially aids in the reduction of BOD and approaches activated sludge. No attempt is made, however, to remove this sludge by settling and much of it will leave by way of the aeration tank effluent.

The aeration tank is usually constructed of reinforced concrete and at such an elevation as to receive the waste by gravity. If the tank is used for preaeration ahead of filtration or activated sludge, a capacity for about 12-hours flow of waste is provided. If it is used as the only means of treatment, the capacity is for the average 24-hour flow. The depth is usually from 6 to 8 feet and some provision is made for the collection and removal of sludge, since some of the solids are sufficiently heavy to settle in spite of the agitation. In large installations a sludge collecting mechanism may be used for this purpose. For smaller operation the bottom may consist of a series of hoppers in which sludge lines are located.

Air is provided by means of a positive pressure-type blower. The quantity of air necessary is about one-half cubic foot per minute (cfm) per pound of BOD per day for the maximum day. Air is applied to the waste by a series of pipelines to which self-cleaning jet nozzles are attached (see Figure 3) or any other type of diffuser except those employing porous plates. If jet nozzles are used ($\frac{3}{8}$ -inch bore), about 3 jets are required for each cfm of air.

BIOLOGICAL FILTRATION

Biological filtration consists essentially of applying the waste to a bed of stone on which a film of active organisms has developed. The standard or one-pass filter is no longer used to any great extent for the treatment of milk waste. This type has been replaced by the recirculating filter because of its efficiency and greater load capacity.^{2,3} The recirculating filter may be single- or two-stage depending upon the degree of removal required. It is preceded by an aeration tank which is also used to receive the recirculated effluent, and is followed by a settling tank for the removal of suspended material from the effluent. Some provision is made for the disposal of the sludge from the aeration and settling tanks, depending upon the size of the operations. A heated digestion tank and sludge beds are most satisfactory for this purpose, but in some cases the cost of such an installation is not warranted due to the relatively small amount of sludge obtained. In these cases it may be ponded or hauled and applied to land.

The design of large units to accommodate the recirculating principle is a matter which should be referred to an experienced engineer. The design is governed mainly by the size of the operation, local conditions of topography, and the desired effluent.

Fill-and-Draw Recirculating Filter

Milk plants vary considerably in size and the treatment process must be adapted to this factor. Figure 4 shows a recirculating filter using the

fill-and-draw principle and adapted for use at very small plants where the daily waste volume does not exceed 3,000 to 4,000 gallons. The tanks may be of wood stave or steel plate construction and are both set above ground. The waste is collected in a small sump and pumped to the equalizing tank which has a capacity to hold the total daily flow but may or may not be equipped for aeration. The waste is pumped over and over the filter at a rate which will provide from 8 to 10 recirculations. The tank is emptied each morning before a new batch of waste is applied.

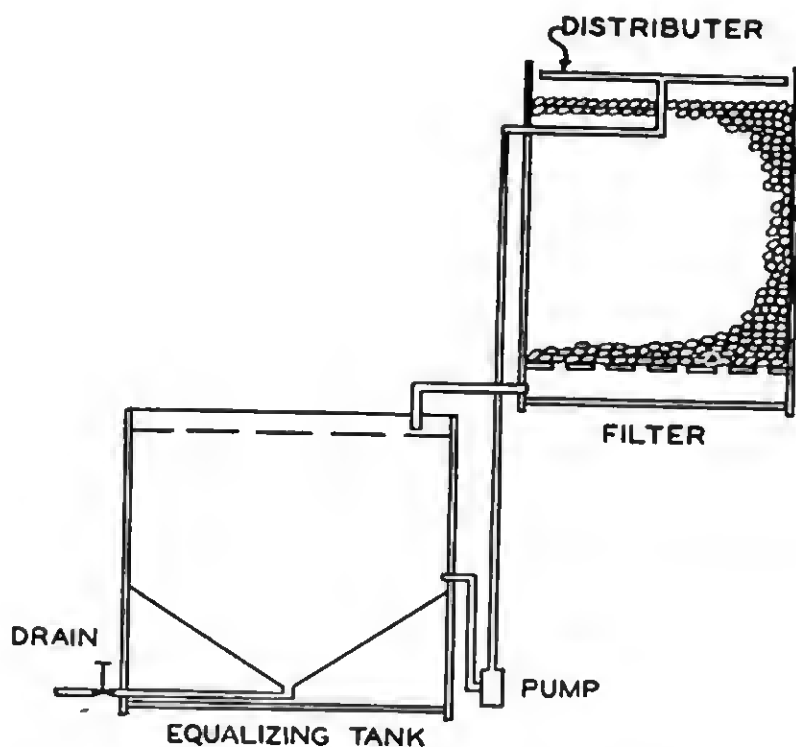


FIGURE 4. Fill-and-draw recirculating filter for the treatment of milk waste

The filter is composed of 3- to 4-inch diameter hard granite stone or slag and is 6 feet in depth. It is supported on a grid located about 6 inches above the bottom of the filter tank. Holes bored just below the grid provide ventilation to the filter. The size of the filter is such as to provide one cubic yard of filter media per pound of BOD per day. Up to 95 per cent reduction in BOD is possible with this batch filtration process, depending upon the number of times the waste is recirculated and its initial concentration.

Recirculating Filter, Single-Stage

The suggested arrangement of units shown in the flow diagram, Figure 5, is adapted to plants where an effluent having a BOD concentration of 70 to 100 ppm is satisfactory. The raw waste enters the aeration tank

through the screen and grit chamber where it mixes with the settled filter effluent. A vertical type centrifugal pump is used to pump the waste to a rotary or other type of distributor which applies it to the filter media. The capacity of this pump is about 8 to 10 times the average rate of flow of raw waste.

The filter bed is 6 feet deep and underdrained in the usual manner. The filter media is composed of hard granite stone or slag, entirely free of sand

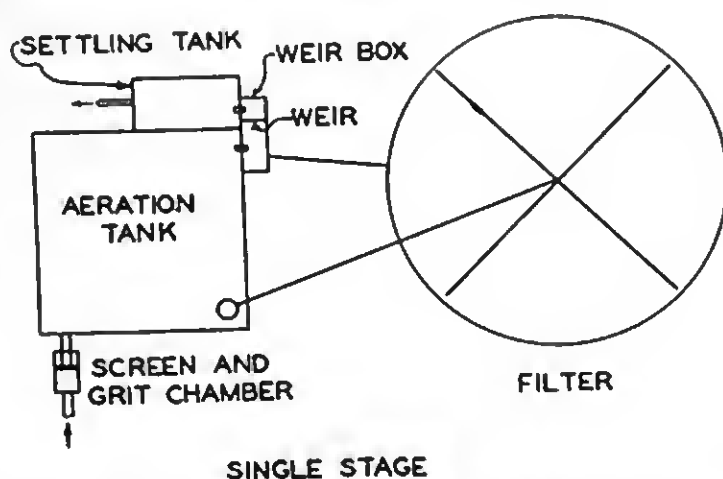


FIGURE 5. Single-stage recirculating filter for the treatment of milk waste

and having no stone smaller than $2\frac{1}{2}$ inches or larger than $4\frac{1}{2}$ inches. The average size is $3\frac{1}{2}$ inches.

The filtered waste flows into a weir box in which the weir is set at the desired level of water in the aeration tank. The rate of flow over the weir is therefore the same as that of the incoming raw sewage. The balance of the filter effluent is returned to the aeration tank.

The waste which flows over the weir is passed through a settling tank having a capacity for the maximum one-hour rate of flow of the raw waste. Provision is made in both the aeration and settling tank for the collection of sludge. In the smaller installations this may be accomplished by constructing hoppers in floors of the tanks and installing sludge lines in these hoppers. In larger installations it may be desirable to install mechanical sludge collection equipment.

The volume capacity of the filter is based on the maximum raw waste BOD load. The recommended loading is one pound of BOD per cubic yard of filter media (1,610 pounds BOD per acre foot). A reduction of from 75 to 80 per cent of the BOD is possible by this process.

Recirculating Filter, Two-Stage

In case the reduction provided by single-stage filtration is not sufficient to meet the requirements, two filters operating in a series may be used.

Figure 6 shows a flow diagram of a two-stage filter. The size or arrangement of the screen, grit chamber, aeration tank or settling tank need not be altered. The waste from the aeration tank is pumped to the first filter and returned to a weir box in which the weir is set at the desired water level in the aeration tank. The capacity of the pump provides for 6 to 8 recirculations.

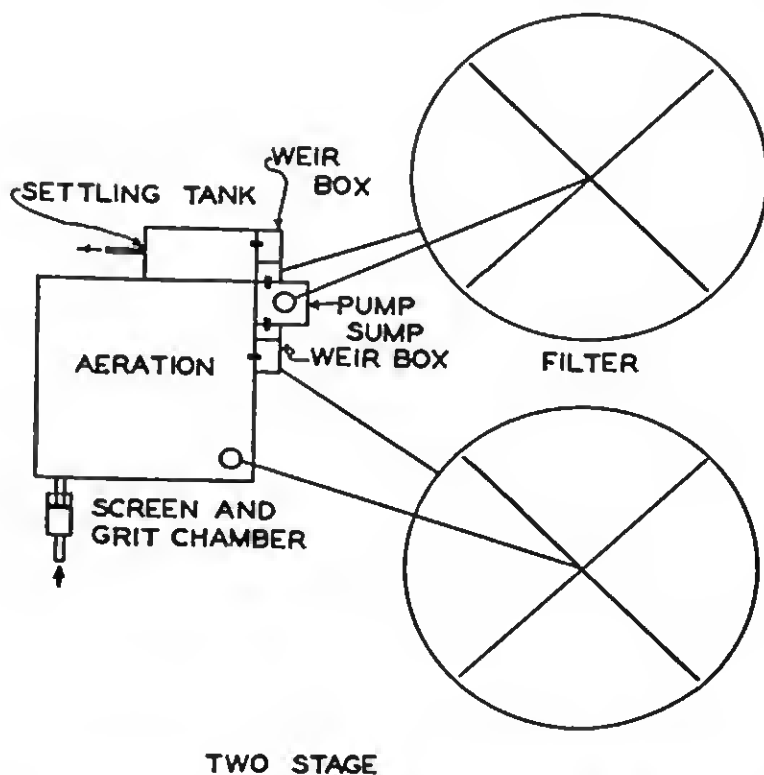


FIGURE 6. Two-stage recirculating filter for the treatment of milk waste

The overflow of the weir enters a pump sump in which a second pump of like capacity is installed. The waste is pumped from this sump to the second filter and returned to a second weir box. The weir in this box is set at the desired elevation of water in the pump sump and at least 6 inches below the weir in the first box. The overflow of this second weir passes through the settling tank to the outfall line. The remaining portion of the second filter effluent enters the pump sump for recirculation.

The tendency in recent years has been toward shallow filters, especially those used for two-stage filtration. Filters 4 feet deep are usually recommended. The stone of the first filter has a diameter between $2\frac{1}{2}$ and 4 inches. It is common practice to use somewhat smaller diameter stone in the second filter, but this often leads to trouble with clogging, especially during winter operation when the efficiency of the entire system is low. Use of the same size stone in both filters is preferred.

A somewhat higher filter loading is used in the design of the first filter than is recommended for the single-stage. Loadings of from 1.5 to 2.0 pounds per cubic yard of media based on the raw waste BOD are generally considered adequate. In calculating the load for the second filter a reduction of 60 to 70 per cent is assumed for the first unit and a loading figure of 0.75 pounds of BOD per cubic yard applied. Using these loadings, the two-stage filtration unit is capable of efficiencies of 90 to 95 per cent and effluents with BOD values below 50 ppm.

ACTIVATED SLUDGE

Experience has demonstrated that the activated sludge process can be successfully used for the complete treatment of milk waste. It consists of developing naturally by aeration of the waste a sludge containing large numbers of organisms which are active in the oxidation of organic solids. These organisms are supplied with sufficient air to maintain a dissolved oxygen content in the liquid media. Air is supplied either by blowers under pressure or by mechanical aerators. Aeration is followed by a period of sedimentation during which the sludge is removed and returned to the aeration unit. Excess sludge beyond that required for adequate oxidation is removed from the process and subjected to anaerobic digestion in a heated digestion tank. There is no need to provide facilities for the disposal of digested sludge since all of the solids are liquefied or gassified in the digestion tank. The supernatant liquor from the anaerobic process is returned to the aerator.

There is evidence, but not definite proof at the present time, that if a sufficient aeration period is provided, there will be no excess activated sludge from the process. Whether or not it is more economical to provide the needed aeration period than to construct a digester for the excess sludge has not been determined. For simplicity of design and operation, however, the elimination of the digester, if possible, is desirable.

Perhaps the largest plant in which the process is demonstrated is that of the Mead Johnson Company at Zeeland, Michigan. This plant uses the Mallory oxidized sludge method of control, but is essentially what is conventionally known as the activated sludge process.^{5,6}

There seems to be a consensus of opinion that this process requires more technical control than is usually available at milk products plants and that it is much more easily upset than is the biological filtration process. Actual experience has proved that this is not the case. This viewpoint has resulted from observations at plants which have not been properly or adequately designed or operated. Properly designed plants which have adequate facilities for providing sufficient air and for the control of the return sludge are not easily upset nor is the control procedure difficult.

The process has certain advantages over filtration such as lower construction costs, less area required for the plant, and much lower effluent BOD values. However, power costs are somewhat higher. It can be adapted to small as well as large milk plants.

There are many types of construction and many possible arrangements of the aeration and settling units which are used to accommodate the activated sludge process and if they provide the essential facilities they should be equal in performance. Steel construction is considered superior



FIGURE 7. Lancaster Iron Works package plant for the treatment of milk waste

to concrete for small installations in that the tanks may be prefabricated. Figure 7 shows a small "package" plant installed by Mallory and the Lancaster Iron Works.⁷ The aeration unit is in the upper portion of the taller tank and the settling tank in the smaller. There is a room under the aeration tank for housing the pumps and blowers.

Figure 8 shows the unusual design of the Mead Johnson plant in which the rectangular settling tanks are contained inside of a large steel circular tank. The aeration compartment is that portion of the circular tank outside of the settling units. The top rim of the circular tank is hollow and is used as a main line air supply. The individual diffuser units are connected to this rim. Aeration is accomplished by means of the self-cleaning nozzles shown in Figure 3. Sludge is returned from hoppers in the settling tank to the aeration compartment by air lifts.

A plant of steel tank construction has been in operation at the Belle

Center Creamery and Cheese Co., Belle Center, Ohio. The plant consists of separate aeration and settling tanks. This plant was designed for 300 pounds of BOD per day and an effluent BOD not to exceed 50 ppm. Actually the BOD of the effluent has averaged about 20 ppm with an average load of 250 pounds per day.

The basic capacity of the aeration unit to accommodate the activated sludge process for the treatment of milk waste is about 80 gallons per pound

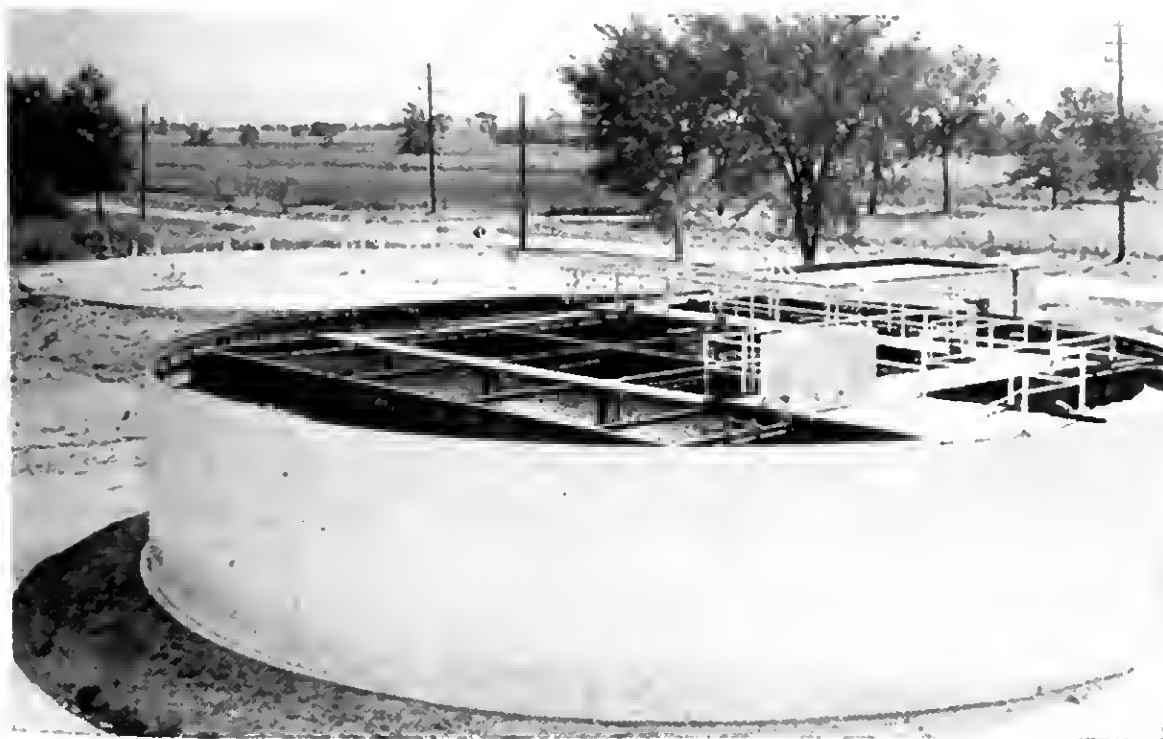


FIGURE 8. The activated sludge plant using the Mallory process at Zeeland, Michigan

of BOD. Air requirements depend upon the nature of the air diffuser units. If self-cleaning nozzles are used, these requirements are approximately one cfm per pound of BOD per day. The rate of return sludge, and the concentration of solids in the return sludge and mixed liquor, are governed by the BOD concentration. For waste having between 800 and 1,200 ppm BOD the return sludge flow for optimum treatment is between 600 and 650 per cent of the waste flow. In this range the concentration of solids in the mixed liquor is from 5,000 to 6,000 ppm. Settling rates and the sludge index are used as a means of control of the process.

Sufficient air capacity must be available in order to maintain dissolved oxygen in both the effluent from the aeration tank and the clarifier. Dual blowers and ample return sludge facilities are important features for the design of units for this process. BOD values below 10 ppm are possible under adequate design and operating conditions.

SUMMARY

The wastes from the processing of milk products consist of washings, spillage, spoiled products, and by-products. By-products and spoiled products should never be discharged to the drain system, but should be utilized for animal feeding or other purposes. Good housekeeping methods aid in reducing the concentration of the wastes and simplify the waste treatment problem. Aerobic processes of waste treatment, biological filtration and activated sludge, are adapted to this waste.

References

1. Dean, W. A., Chairman Task Committee on Dairy Waste Disposal, *Assoe. Bull. on Milk Ind. Foundation*, 39th Year, No. 2 (Dec. 1946).
2. Eldridge, E. F., *Michigan State College Eng. Expt. Sta. Bull.*, 71, 49 (1936)
3. Eldridge, E. F., *Sewage Works Eng.*, 2, 599 (1940).
4. Eldridge, E. F., "Industrial Waste Treatment Practice," New York, McGraw-Hill Book Co. (1942).
5. Eldridge, E. F., *Mich. State College Eng. Expt. Sta. Bull.*, 94 (1942)
6. Mallory, E. B., *Water Works & Sewerage*, 89, 143 (1942).
7. Mallory, E. B., *Water Works & Sewerage*, 87, 102 (1940).
8. Reinke, E. A., *Calif. Sewage Works J.*, 1, 3 (1928).
9. Trebler, H. A., and Harding, H. G., *Ind. Eng. Chem.*, 39, 608 (May 1947).
10. Trebler, H. A., Ersberger, R. P., and Roland, C. T., *Sewage Works J.*, 10, 868 (1938).
11. Trebler, H. A., *Proc. of First Ind. Waste Util. Conf.*, Purdue Univ. (Nov. 1944)

4. Canning, Freezing and Dehydration

N. H. Sanborn

*Research Laboratories, National Cannery Association,
Washington, D.C.*

One of the major industries in the United States is the preservation of food. Among the various units comprising this industry, the canning industry had an output in 1946 valued at approximately \$1,000,000,000, and the frozen fruit and vegetable industry one of approximately \$200,000,000. Geographically, approximately 3,000 canning plants are located in 47 states and in each of the territories of the United States. It is estimated that there are about 250 plants engaged in freezing fruits and vegetables, many of which are operated in conjunction with canning. Statistics on the output of the major vegetable and fruit crops of these industries for 1946 are given in Table 1.

Experience during two wars has demonstrated that the demand for dehydrated vegetables is largely a matter of feeding troops. During the 1943-44 and 1944-45 periods the production of dehydrated vegetables amounted to 190 million pounds per year. The United States Department of Agriculture has estimated that a potential civilian market of about 25 million pounds of dehydrated vegetables could be developed. Of this amount, 14 million pounds would consist of onions and garlic for which there has always been a good demand from manufacturers of prepared products. It was estimated that a market for 8 to 10 million pounds of dehydrated white potatoes would continue compared with a wartime peak production of 125,595,000 pounds. An expanding market for soup mixes prepared from dehydrated vegetables was anticipated. Potato wastes from the dehydration industry undoubtedly will remain as the most difficult waste requiring treatment or disposal.

SOURCES AND CHARACTERISTICS OF WASTES

Large volumes of water are used by the canning, freezing and dehydration industries in the washing of produce, blanching, hydraulic movement

INDUSTRIAL WASTE TREATMENT

TABLE 1. 1946 VEGETABLE, FRUIT AND FISH PACKS

Vegetables	No. of Cases Canned*	Lbs Frozen
Asparagus	4,443,000	28,316,074
Beans, dry	37,000,000	
Beans, green and wax	17,102,000	40,974,804
Beans, lima	1,718,000	50,082,682
Beets	7,248,000	
Broccoli		25,788,855
Brussels Sprouts		13,521,280
Carrots	3,418,000	9,069,314
Cauliflower		13,236,775
Corn	32,526,000	44,722,347
Peas	39,929,000	140,602,919
Peas and Carrots		7,186,108
Pumpkin and Squash	3,235,000	10,008,776
Rhubarb		10,566,207
Sauerkraut	6,076,000	
Soups	46,000,000	
Spinach	7,200,000	38,185,104
Succotash		3,409,548
Sweet Potatoes	3,085,000	
Tomatoes	20,995,000	
Tomato Juice	30,525,000	
Tomato Pulp	9,356,000	
Miscellaneous	58,000,000	14,329,410
Fruits		
Apples and Apple Sauce	12,141,000	78,219,867
Apricots	10,802,000	43,571,459
Berries	1,032,000	154,588,506
Cherries, Sour	3,086,000	
Cherries, Sweet	2,082,000	
Cranberry Sauce	6,312,000	
Fruit Cocktail and Salad	7,832,000	
Grapefruit Segments	2,722,000	
Olives	1,700,000	
Peaches	20,755,000	65,374,216
Pears	5,547,000	
Pineapple	10,237,000	
Prunes	3,576,000	14,106,368
Miscellaneous		75,374,216
Fruit Juices		
Apple	3,524,000	
Citrus	54,617,000	
Pineapple	8,207,000	

*Actual cases, generally 24 cans per case.

of products within factories, and in maintaining sanitary conditions by washing equipment and floors. The larger plants may discharge 1,000,000 gallons of waste per day. These wastes consist largely of carbohydrates in suspension and solution.

Flow diagrams showing the sources of waste in the canning of peas, corn, tomatoes and grapefruit are presented in Figures 1, 2, 3 and 4. Water

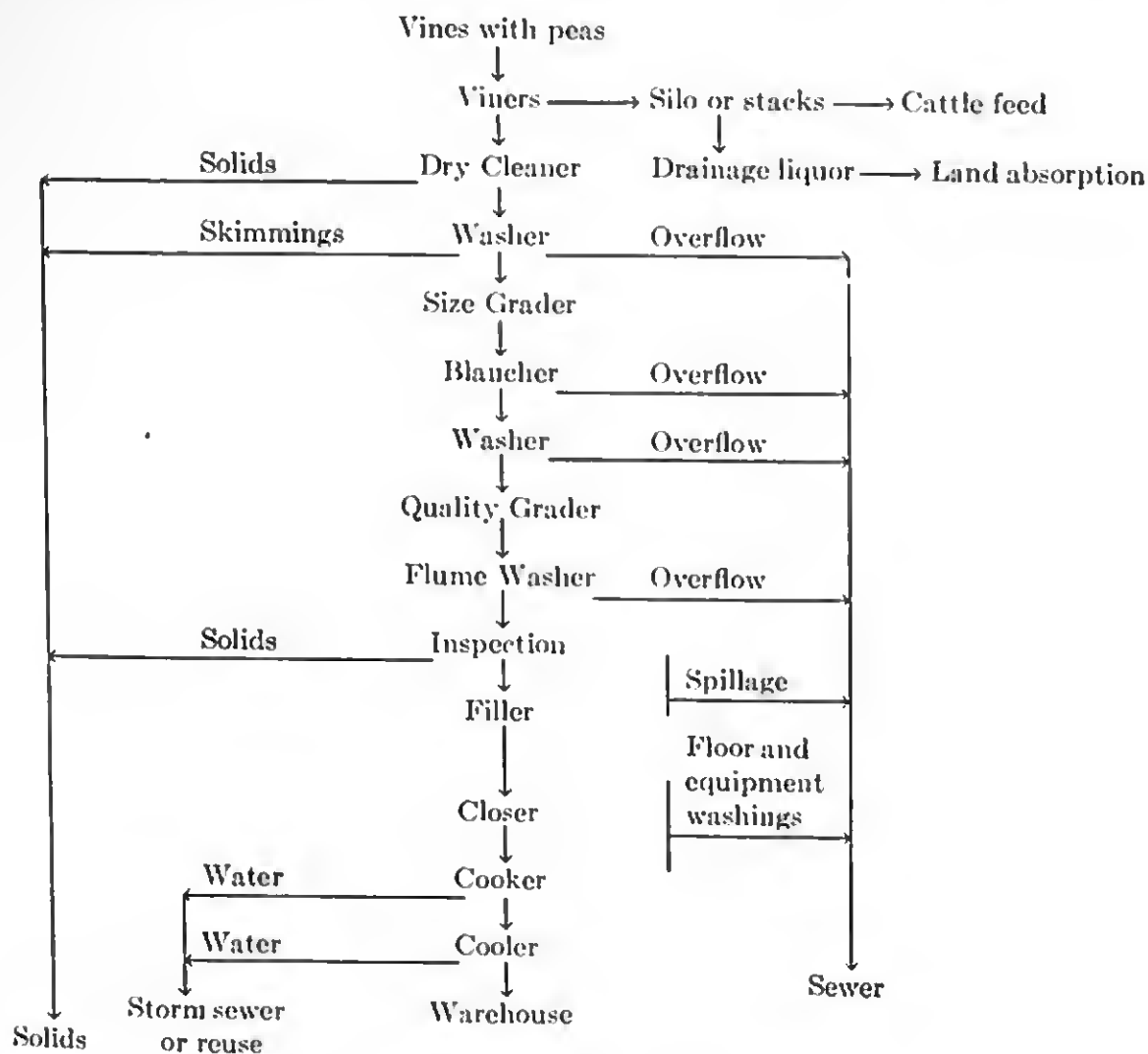


FIGURE 1. Flow diagram of pea canning

used in the cooling of heat-processed containers usually contains little or no organic matter. In most cases it is separated from other factory wastes and disposed of without treatment. Under such conditions it is not included as part of the flow of contaminated factory waste water. At those plants where a disposal problem develops and can cooling water has not been segregated, separate disposal of the latter is indicated to reduce the volume of waste requiring treatment.

The volume and characteristics of waste waters vary enormously among the various products packed, among packers of the same product, and from day to day in the same plant. It is obvious to anyone familiar with these wastes that it is essential to study each individual case rather than to rely on published data in designing a treatment plant. Some conception of the variability of these wastes may be gained from the data assembled

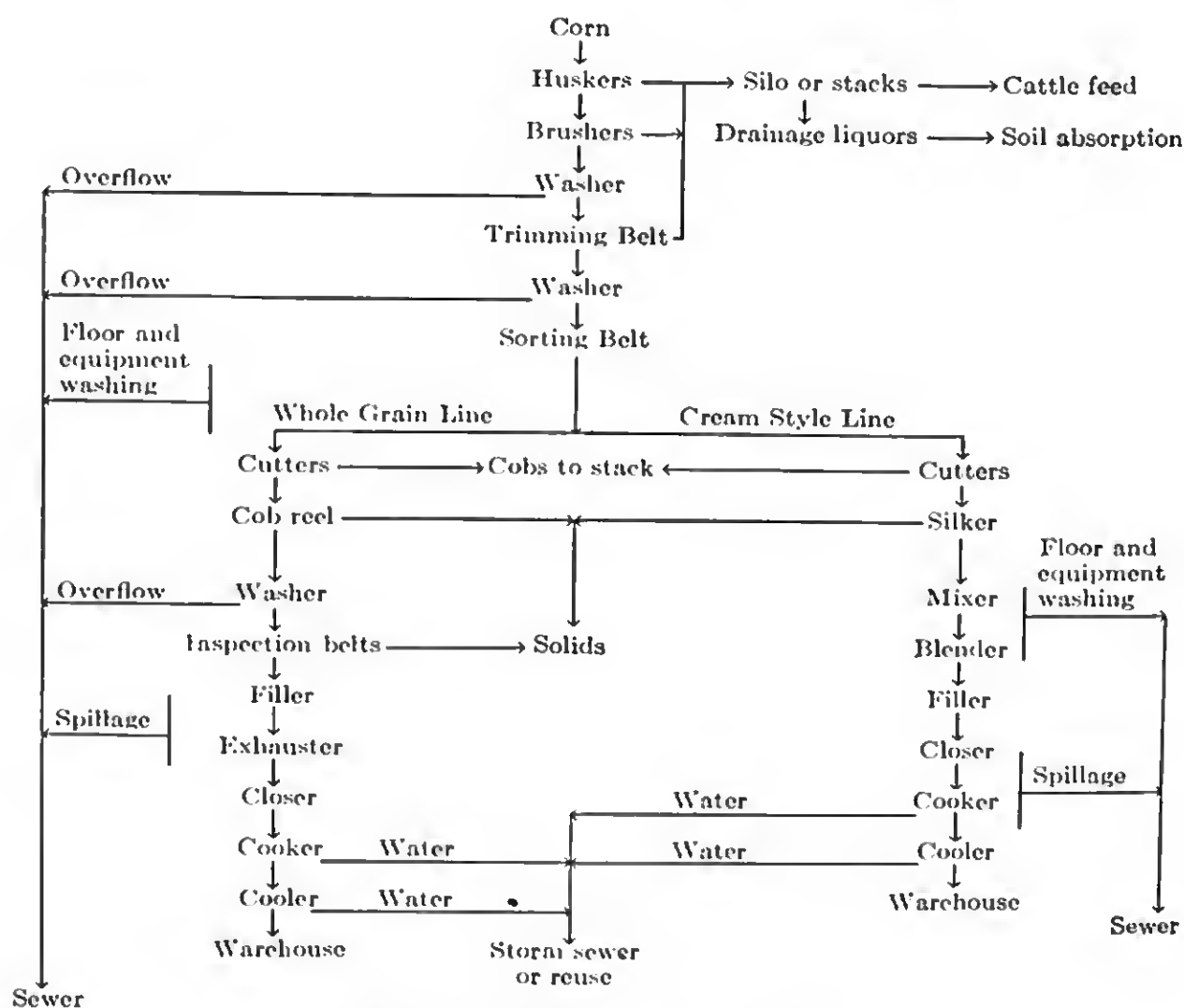


FIGURE 2. Flow diagram of corn canning

from many sources and presented in Table 2. Details concerning the collection of samples are frequently lacking. It is believed that most, if not all, of the data were obtained after screening.

A limited amount of data are available on some of the waste characteristics from specific operations. Biochemical oxygen demand values are given in Table 3. No attempt has been made to collect and treat separately certain strong wastes such as blancher water. In general, it does not appear

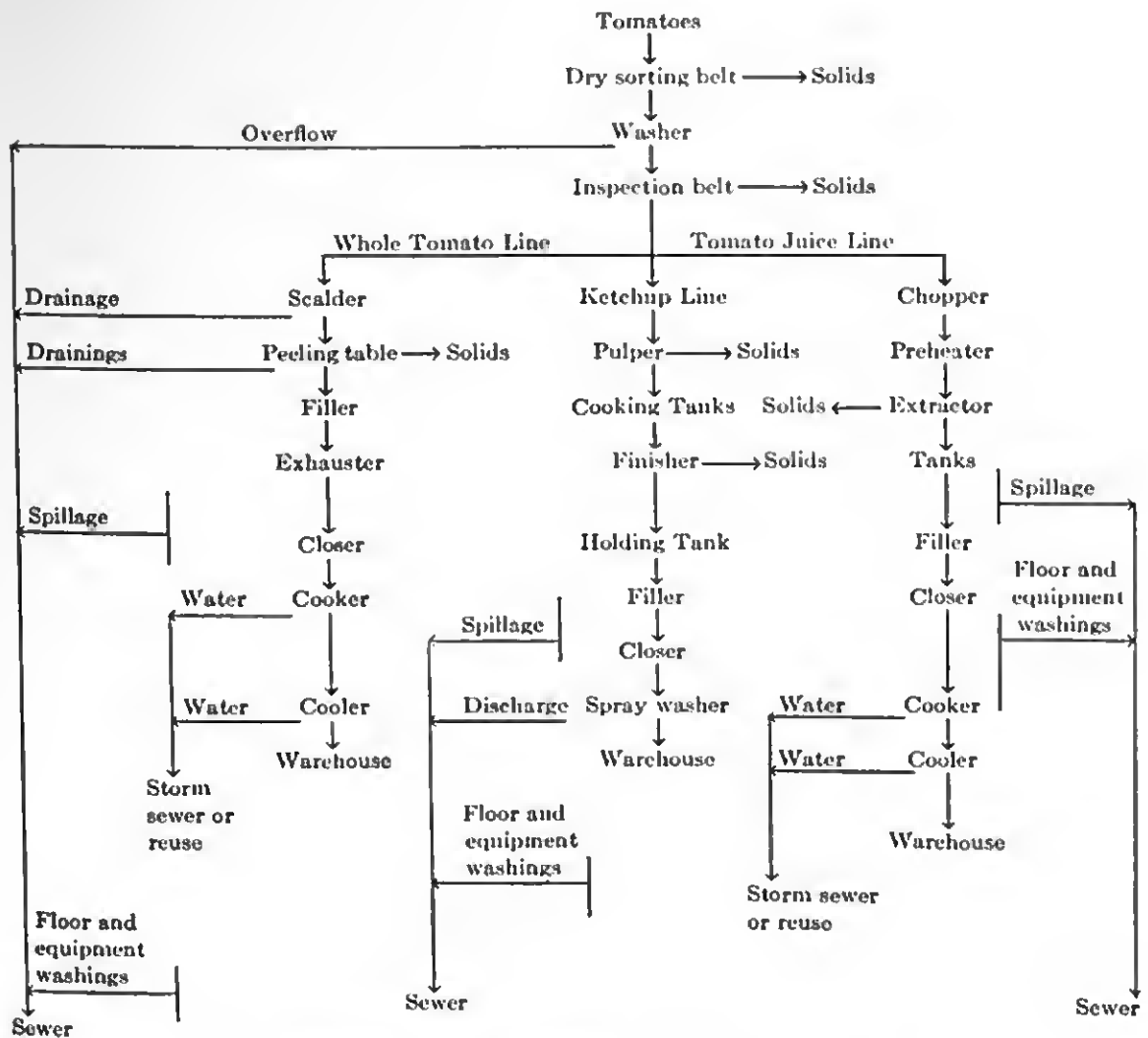


FIGURE 3. Flow diagram of tomato canning

feasible to provide for separate collection and treatment. The characteristics and treatment of ensilage stack liquor is discussed in a following section.

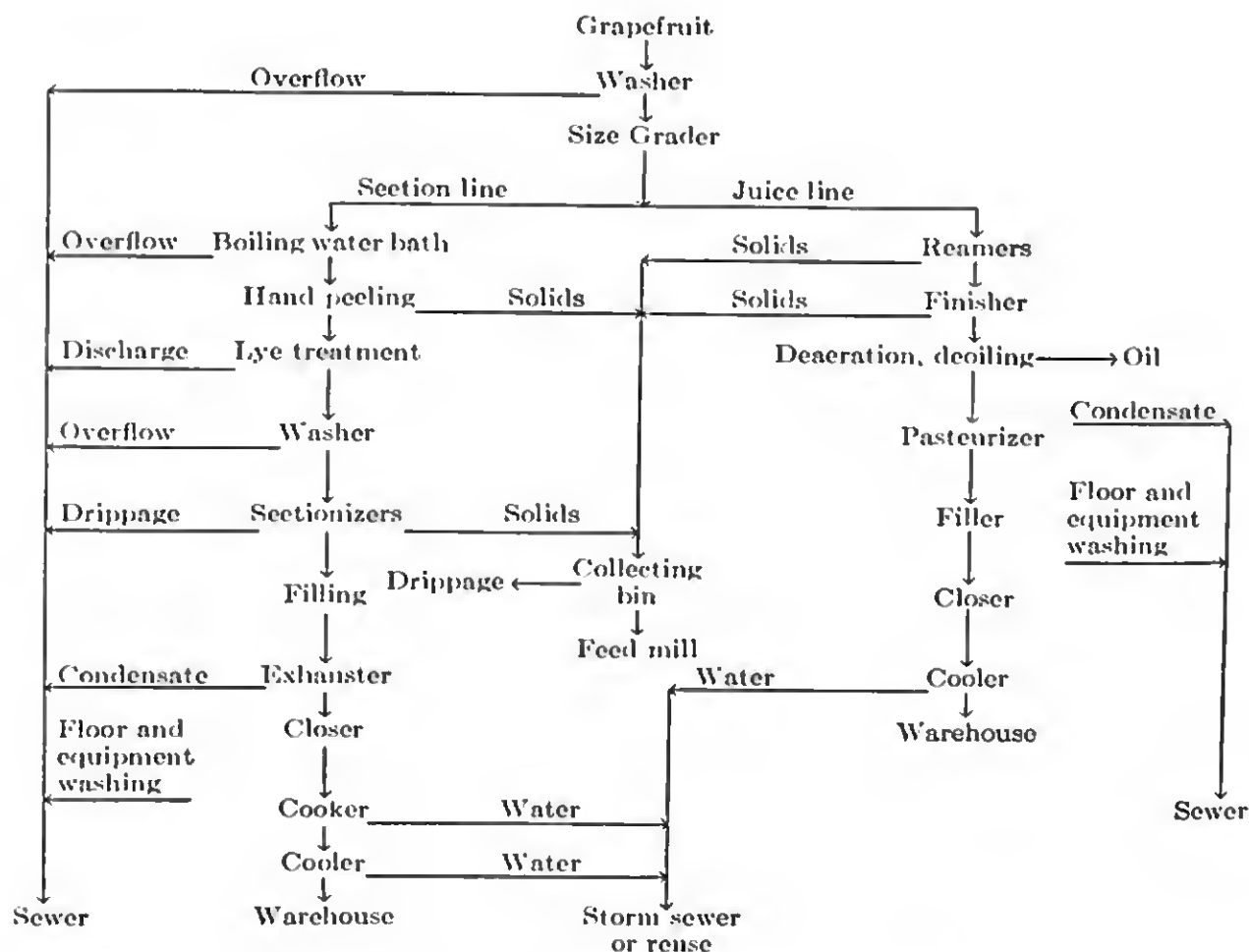


FIGURE 4. Flow diagram of grapefruit canning

The transportation of solids wastes by separate flumes to waste screening units offers certain advantages from the standpoint of conveyance but materially increases the strength of liquid wastes which are to be disposed of. Solids collected within the plant should be handled separately in appropriate containers or by mechanical conveyors. For the same reason both comminution and dewatering of solids are undesirable practices. The importance of spillage of syrup, product of solid wastes is sometimes not recognized.

TREATMENT OF LIQUID WASTES

Canning, freezing and dehydrating operations are largely seasonal in nature and occur for the most part during the summer months when stream

TABLE 2. VOLUME AND CHARACTERISTICS OF CANNERY WASTES

Product	Volume Per Case (Gals)	5-Day BOD (ppm)	Suspended Solids (ppm)
Apples, sauce		1,685-3,453	
Apricots	57-80	200-1,020	260
Asparagus	70	100	30
Beans, green or wax	26-44	160-600	60-85
Beans, lima	50-257	189-450	422
Beans, baked	35	925-1,440	225
Beets	27-65	1,580-5,480	740-2,188
Carrots	23	520-3,030	1,830
Corn, cream style	24	623	302
Corn, whole kernel	25-70	1,123-6,025	300-4,000
Cherries, sour	12-40	700-2,100	20-605
Grapefruit	5-56	310-2,000	170-287
Mushrooms	6,600*	76-390	50-242
Peaches	1,300-2,600*	1,350	600
Pears	1,300*	2,250-4,700	1,200-6,700
Peas	14-56	380-4,700	272-400
Potatoes, sweet	3,500*	295	610
Potatoes, white		200-2,900	990-1,180
Pumpkin	20-42	2,850-6,875	785-3,500
Sauerkraut	3	6,300	630
Spinach	160	280-730	90-580
Tomatoes, whole	3-15	570-4,000	190-2,000
Tomatoes, juice or products	38-100	178-3,880	170-1,168

* per ton.

flows are at a minimum and temperatures and biological activity are at a maximum. The wastes are far from uniform with respect to both quantity and quality. These industries are generally located in or near small towns with inadequate or no municipal disposal facilities. These and other factors, together with the continued expansion in the canning and freezing industries, have accentuated the problem of the disposal of liquid wastes. The discussion which follows will be confined to cannery wastes, since these wastes are typical of those from the freezing and dehydrating industries. The basic methods of preparation and handling which involve the production of wastes are the same. No published information has appeared on wastes from freezing operations, and few reports on wastes from food dehydrating plants are available.^{11,19,25}

The type of treatment most suitable for a particular plant will depend upon the volume and characteristics of each type of waste produced, degree of treatment required, number and duration of packing periods, area and topography of land available for the treatment plant, possibilities of utilizing local municipal treatment works if any exist or are contemplated, and financial considerations. With respect to the latter, consider-

INDUSTRIAL WASTE TREATMENT

TABLE 3. BOD OF WASTES FROM SPECIFIC OPERATIONS

Peas	(ppm)
Pea Washer	3,700
Blancher Overflow	13,815
Blancher Dump	34,490
Ensilage Stack Liquor	35,000-78,000
Corn	
Cob Washer	2,800
Whole Kernel Washer	7,000
Ensilage Stack Liquor	22,000-33,000
Kidney Beans	
Soak Water	10,500
Blancher	3,600
Cherries, sour	
Pitter Drillage	38,000-55,000
Pit Flume Water	950-3,330
Grapefruit, sections	
Fruit Wash Water	20-110
Peeling Table	380
Sectionizing Tables	2,480
Exhaust Box Overflow	1,000
Floor Wash Water	4,000
Peel Bin Drillage	50,600

ation must be given to the fact that most food processors of the type under discussion operate on a seasonal basis which does not justify the capital expenditure for treatment that could be borne by a plant operating throughout the year. After obtaining basic information with regard to the waste and existing local conditions, treatment by one or a combination of the following methods can be considered: screening, chemical precipitation, biological treatment, discharge to a municipal treatment plant, irrigation fields or discharge to an impounding lagoon.

A tabulation of the extent to which these methods of treating liquid cannery wastes were actually in use in one state during 1947 is revealing:

- (1) Screening: 61
- (2) Chemical precipitation:
 - (a) Fill and draw system: 21, of which 7 constituted pretreatment prior to discharge to municipal treatment plants. The balance discharged directly to streams
 - (b) Continuous system: 2. One discharged to a municipal treatment plant
- (3) Biological filters (cannery operated): None
- (4) Discharge directly to municipal treatment plants after screening: 30
- (5) Irrigation fields: none

(6) Lagoons:

- (a) Sodium-nitrate treated: 33, of which 2 were utilized as equalizing basins for regulated discharge to municipal treatment plants
- (b) Lime treated: 1
- (c) Untreated: 10

It will be noted that in this center of canning activity there are no cannery operated treatment plants using biological filtration, an expensive and questionable method for the treatment of seasonally produced wastes. Absence of soil of suitable porosity has prevented the utilization of economical irrigation fields. This state has permitted a reasonable usage of stream dilution following appropriate pretreatment. In some 40 cases it has been possible to utilize municipal sewage works for further purification. Complete elimination from streams has been obtained, when necessary, by the use of lagoons.

Screening

Efficient screening of all liquid wastes carrying any screenable organic material is essential unless the wastes are discharged into isolated lagoons where odors are no problem. Failure to screen wastes completely has given cause for complaint in many instances, such as in receiving bodies of water otherwise capable of absorbing the waste, in overloading lagoons treated for odor control, overloading digester capacity of municipal treatment plants, and in clogging filter distributor arms when the waste is received at the treatment plant in a separate sewer which by-passes the primary settling tank.

The screening unit should be located as near as possible to the point at which the several waste lines are brought together to minimize mechanical disintegration of soft solids into particles small enough to pass through the screen and to minimize leaching of soluble constituents into the liquid phase.

Mechanically operated screens of either the rotating or vibrating type should be used. Rotating screens require less mechanical attention. Vibrating screens have a much higher capacity per square foot of screen cloth and deliver comparatively dry and compact screenings. Because of the rapid rate of vibration the screen cloth must be kept in tension, otherwise splitting will occur.

A 20-mesh screen is recommended for most wastes. Screens with openings as large as $\frac{1}{8}$ inch may be permitted in special cases such as in discharge to large flowing bodies of water, tidal estuaries or to municipal plants where the volume of waste is small in comparison with the flow of domestic sewage. Screens must be kept clean to prevent clogging. Rotary

units are equipped with sprays. Vibrating screens should be brushed frequently with a detergent. It is important for proper safeguards to be provided to prevent screenings from falling back into the flow of screened liquid waste, a detail that is frequently neglected.

The use of stationary screens alone cannot constitute adequate screening. If constructed of 20-mesh wire or finer they quickly become clogged. If the wire cloth has openings large enough to permit a free flow only the coarser solids are retained. Stationary screens installed after mechanical screening provide a factor of safety in the event of difficulties at the primary screening unit.

Chemical Precipitation

The seasonal nature of most food processing operations, lack of municipal treatment facilities, and high cost of complete biological treatment have stimulated investigations on chemical precipitation as a method of treatment.^{5,14,15,23,30,31,38,46,50} Pretreatment by screening is necessary since the larger floating solids cannot be removed by a chemical floc. Small solids which pass through the screen and organic materials such as starch and proteins present in colloidal suspension can be removed almost completely by chemical precipitation in the so-called "batch" or "fill-and-draw" system. Soluble organic solids such as sugars which are in true solution cannot be so removed. The relative proportion of suspended, colloidal and soluble solids as determined by the type and condition of products packed, variations in methods of factory preparation, and manner of handling solid wastes will determine the percentage BOD reduction. As a method of treatment, chemical precipitation is not as popular now as it was some 15 to 20 years ago, because of the increased demand for more complete treatment. Chemical precipitation plants have been installed principally to treat pea and corn wastes, and to a lesser extent, tomato, beet, carrot, kraut, apple and cherry wastes.

Experience has shown that the primary considerations in chemical treatment are (1) raising the pH of the waste to the range of 10 to 11, (2) formation of a large rapidly settling chemical floc, and (3) prompt and complete removal of settled floc. The first of these conditions is met by the use of lime. Experience has demonstrated that maximum clarification is obtained with the use of a high calcium hydrated lime. With beets, carrots, tomatoes, and possibly other products, lime alone is capable of effecting a good BOD reduction. However, the floc produced is of small size and the rate of settling comparatively slow. The addition of other precipitants, particularly the various iron salts and, to a lesser degree, alum, produces large rapid-settling flocs. Excellent results have been obtained experimentally with zinc chloride but this salt has not been used

commercially because of its higher cost. Of the several iron salts, ferrous sulfate is universally used in factory-operated chemical treatment plants because of the ease of handling and storage under conditions existing at food plants.

The first chemical treatment plants to be installed were of "continuous" or "flowing-through" design of the general type described by Baker, Warrick and Smith.⁵ In this method chemical coagulants are added to the screened waste in mixing channels leading to a hopper bottom settling tank. Sludge is removed by either gravity flow or by pumping.

Experience with these installations disclosed certain operating difficulties. The frequent changes in waste characteristics made it difficult to secure optimum chemical dosage. Inability to remove sludge completely results in a marked decrease in efficiency.

These difficulties were met by the "fill-and-draw" or "batch" method of chemical precipitation.⁴⁶ Figures 5 and 6 present the recommended layout. A minimum of two tanks is required. Figure 7 shows a view of a plant constructed with steel tanks. Sludge drying beds are shown in the foreground.

Treatment consists in pumping screened waste to one of the several treatment tanks. When the tank is full or nearly full, the estimated lime dosage is added over a period of 5 to 10 minutes with the stirring mechanism in operation. The second coagulant, usually ferrous sulfate, is added slowly until a large floc is formed which shows a tendency to settle rapidly even during agitation. The stirring mechanism is then stopped. The operator can judge by the appearance of the floc in the tank or in a glass jar, and by taking a pH reading, whether the optimum treatment has been obtained. If not, appropriate adjustment is made. The floc is allowed to settle, after which the clear supernatant is discharged through a swinging outlet pipe, followed by gravity discharge of the sludge to drying beds.

Dosage rates per 1,000 gallons of screened waste are approximately as follows:

Beets	10 lbs lime, 4 lbs ferrous sulfate
Carrots	5 lbs lime, 1 lb ferrous sulfate or 8 lbs lime only
Corn	9 lbs lime, 8 lbs ferrous sulfate
Peas	7 lbs lime, 3 lbs ferrous sulfate
Sauerkraut	15 lbs lime, 6 lbs alum
Tomatoes	4 lbs lime, 1 lb alum

Corn waste is the most difficult to clarify because of the quantity of polysaccharides in colloidal suspension. Experience with corn waste has shown that it is more effective to add ferrous sulfate in increments (stage precipitation) than in a single application. This phenomenon may be explained on the basis of the following theory: When an amount

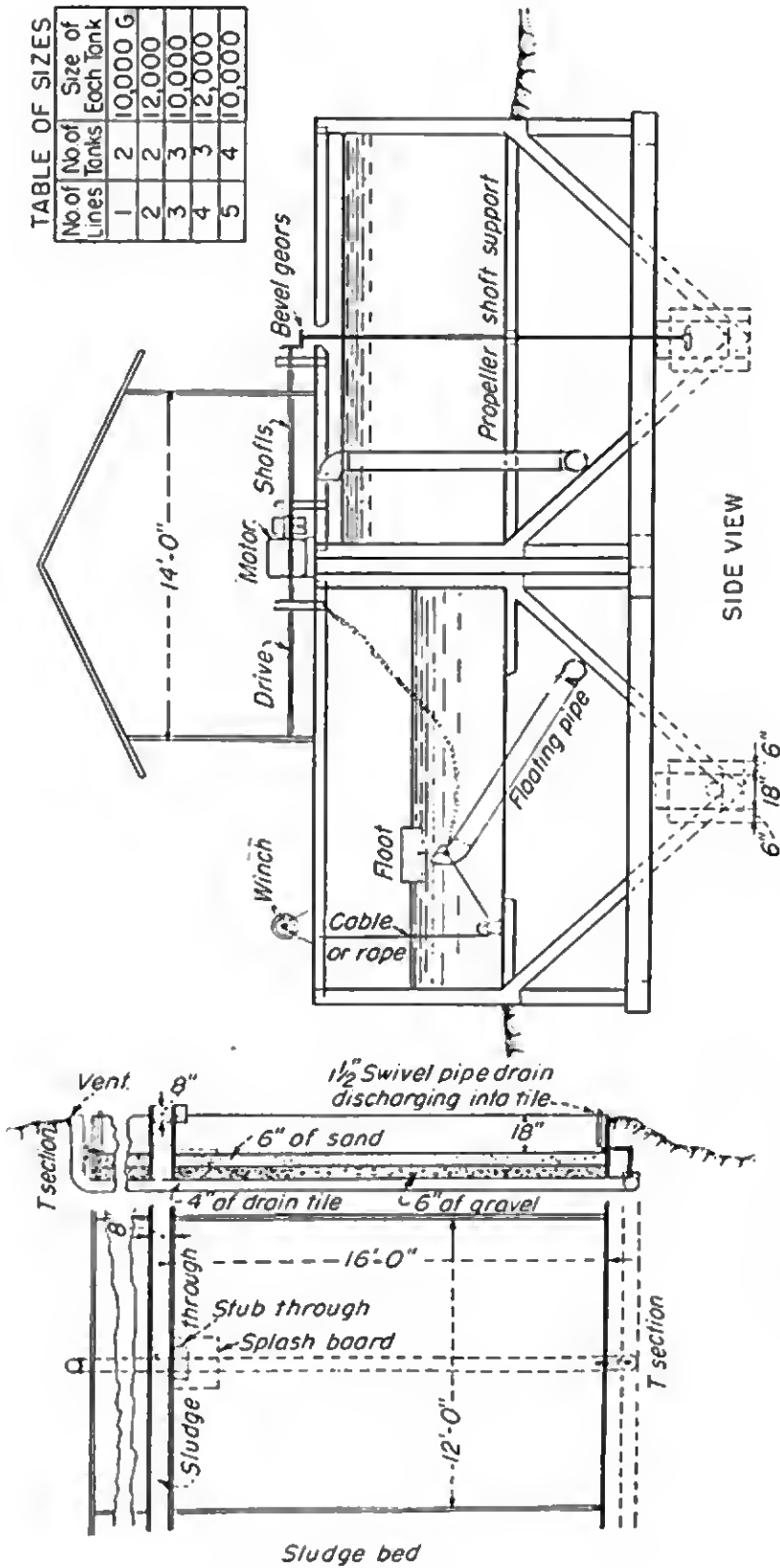
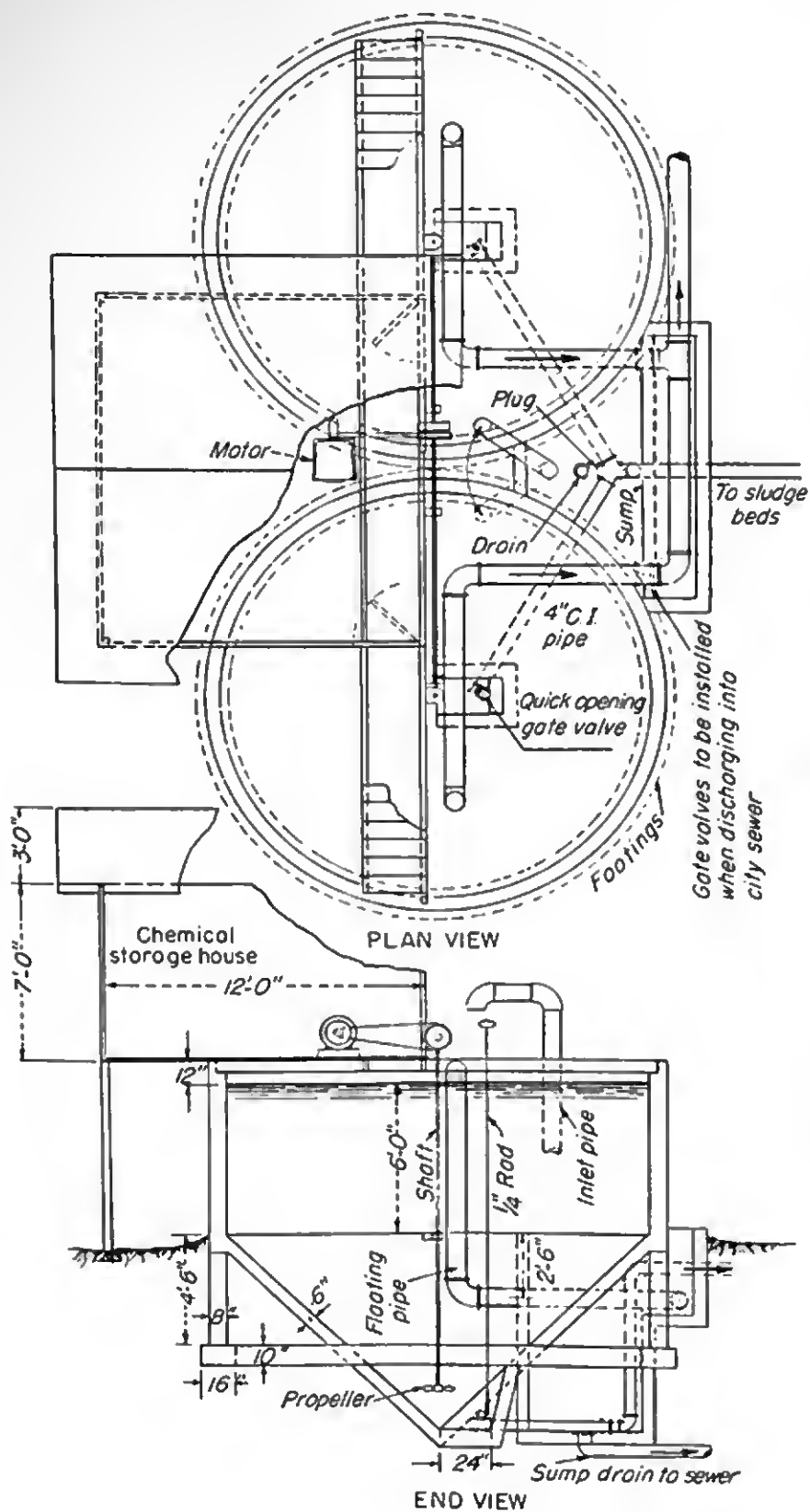


FIGURE 5. Layout for chemical treatment of cannery waste (side view and sludge bed)



of ferrous sulfate previously shown to be sufficient to produce a water white supernatant by stage precipitation is added to a limed waste in a single dose, it fails to clarify because the surface of the floc becomes coated with colloidal starch. The ability of the floc to adsorb additional starch is thus destroyed. When, however, the same amount of ferrous sulfate is added slowly, fresh surfaces are built up on the flocs, which then adsorb additional amounts of colloidal starch. The adsorption



FIGURE 7. Chemical treatment, "fill-and-draw" system. Sludge beds in foreground.

capacity of the surface of a floc is limited and must be renewed by the addition of more of the floc-forming material. The large flocs settle rapidly.

An analysis of published and unpublished data on the efficiency of chemical precipitation leads to the conclusion that, on the average, approximately 50 per cent of the 5-day BOD is removed in full-scale plant operation. With some products experienced operators can obtain higher efficiencies. A comparison of the efficiencies obtained in treating 10,000- to 20,000-gallon batches of waste compared with experimental batches ranging up to 100 gallons has shown that the more gentle methods of mixing which are possible in the smaller batches result in higher BOD removals. Possibly, control facilities to permit variable mixing propeller speeds to secure an initial quick mix, followed by flow flocculation, as well as a study of the size, type, location and use of more than one propeller would lead to increased efficiencies. The latter feature incorporated in two 11,350-gallon tanks treating corn waste gave an average BOD reduction of 79 per cent. Further investigations would be desirable.

Chemical precipitation produces some 10 to 15 per cent by volume

of sludge. When precipitation is carried out at a pH of 10 or higher, the sludge will dry within 7 days without producing an odor, if applied to properly constructed sand beds.

Biological Filtration

Most of the available information on biological filters operating solely on vegetable and fruit wastes has been obtained from experimental units.^{2,12,24,28,30,31,43,44,46} Results reported indicate that these wastes are amenable to standard or high-rate biological treatment. The short seasonal operating periods, the variability of hours of factory operation, and the fluctuating characteristics of the wastes are factors which make the evaluation of biological treatments difficult.

The simple fact that most vegetable and fruit canning or freezing operations are of necessity seasonal almost precludes successful treatment by biological methods in disposal plants operating solely on seasonal wastes. Consider, for example, the processor who packs only peas and corn. The season for peas lasts for a period of about 4 weeks. The treatment plant would remain idle for a period of about one month prior to the treatment of corn wastes, which would then continue approximately 5 weeks. Unless the treatment plant has facilities for recirculation of an artificial conditioning medium prior to and between packs, maximum biological efficiency cannot be obtained until each packing period is practically completed. Recirculation of an artificial conditioning medium is expensive and at best of limited value.

From experimental studies conducted in New York³⁰ on pea, green bean and tomato wastes the following conclusions were drawn:

- "(1) Trickling filters when operated at 0.5 mgad rate throughout the working day are effective in removing 80 to 95 per cent of the organic matter in canning wastes, measured in terms of the 5-day BOD and this treatment is adequate when the final dilution is not less than 1 to 5.
- "(2) Trickling filters when operated at the rate of 2 mgad throughout the working day are effective in removing 50 to 70 per cent of the organic matter and this treatment is adequate when the final dilution is not less than 1 to 20, provided serious pooling can be prevented."

Von Loeseeke, *et al.*,⁴⁴ after investigating several methods for the treatment of citrus canning wastes concluded that "trickling filtration offered the most promising solution for the disposition of citrus-cannery effluents in those cases where flooding of isolated tracts of land or emptying into tide water rivers or large bodies of water is impractical." The

pilot unit consisted of a single-stage filter with secondary settling. Their summary of data for the filter is given in Table 4. The citrus canning season extends over a period of approximately 6 months. The length of this operating period justifies consideration of biological treatment.

TABLE 4. SUMMARY OF DATA FOR TRICKLING FILTER OPERATING ON CITRUS WASTE
(Dosing, Intermittent)

Operating Period	12/5 to 1/9	1/18 to 3/7	4/10 to 4/25
Equiv. dosing rate (mg/papd)	2.16	1.38	1.56
Mean air temp. (°F)	63.6°	68.9°	68.6°
Temp. infl. (°F)	84.3°	87.4°	89.8°
Temp. effl. (°F)	64.2°	65.5°	70.1°
Oxygen-consumed value (ppm)			
Infl.	762	755	1021
Effl.	309	113	184
Settling tank	279	99	131
5-Day BOD (ppm)			
Infl.	641	633	876
Effl.	302	68	108
Settling tank	291	79	101
pH Value			
Infl.	6.49	6.25	6.48
Effl.	7.04	7.33	7.42
Settling tank	7.02	7.27	7.33
Over-all reduction in oxygen-consumed value (%)	63.4	86.8	87.1
Over-all reduction in 5-day BOD (%)	54.6	87.5	88.4

High-rate biological treatment of cannery wastes has been studied on experimental units in Wisconsin and Indiana. The Wisconsin studies⁴⁶ led to the following conclusion:

- “(1) Biological treatment of screened cannery waste is effective where means can be provided for building up a satisfactory growth on the filter prior to the canning season.
- “(2) With six passes of screened waste through a trickling filter built of crushed rock, 2½ to 3 inches in size, 8 feet deep, and operating at 458 gallons per square foot of filter surface (20 mgad) per day, the oxygen demand of beet waste was reduced 60 per cent, corn waste 70 per cent and tomato waste 73 per cent. The waste may be effectively treated by continuous dosage of the filter and recirculation of a portion of the filter effluent, the efficiency increasing with the amount of recirculation. Settling of the filter effluent in a suitable tank for a period of one hour further reduced the oxygen demand 10 to 15 per cent.”

Indiana tests² involved treatment of screened tomato wastes at the rate of 30 mgad both with and without pretreatment by chemical precipitation. The treatment plant consisted of primary sedimentation, high-rate filtration, and secondary sedimentation. Using screened waste without chemical treatment and having an initial average BOD of 999 ppm, an over-all BOD reduction of 59.5 per cent was obtained. During several testing periods when chemical pretreatment was employed, the average initial BOD's ranged from 754 to 1,010 ppm, and the over-all BOD reductions obtained were 75.5 to 78.6 per cent. It was found that small size filter media (1 to 2½ inches) cannot be used in high-rate filters on cannery waste. The filter did not clog with medium ranging from 2½ to 4 inches in size. With regard to the recirculation ratio it was concluded that "the increased efficiency of the high-rate filter when operated at a return ratio of three to one rather than a return ratio of one to one does not apparently justify the additional cost."

Dickinson,¹² in experimental work done in England, concluded that dilution of settled cannery waste with a sufficient proportion of filter effluent to give a mixture having an average BOD of 200 ppm, and applied to a filter at a rate of 100 gallons per cubic yard per day for a maximum period of 10 hours, followed by recirculation of the effluent for 14 hours would permit satisfactory treatment of strong wastes. In American practice, canning and freezing plants operate two or three shifts per day for extended periods of time.

Wastes from non-seasonal packs could, at least theoretically, be treated satisfactorily by biological filtration. Standard single-stage filters would appear suitable for relatively weak wastes applied at a loading of 80 cubic feet of filter medium per pound of 5-day BOD.

There is a need for a systematic evaluation of the several biological systems for the treatment of food wastes from plants operating throughout the year. Two-stage biological filtration with recirculation offers interesting possibilities but has not been investigated with respect to fruit or vegetable food processing wastes. Some wastes are deficient in nitrogen and possibly other nutrients necessary for the proper development of filter flora. Addition of nutrients might materially enhance filter efficiencies. Research on this phase is lacking. At present, the situation with respect to biological treatment for factory operated treatment plants is one of uncertainty.

Treatment at Municipal Plants

The treatment of food wastes at municipal treatment plants, so long as their capacity is not exceeded, is an ideal solution. Experience at municipal sewage works indicates that fruit and vegetable wastes, *per se*, do

not contain organic substances inimical to normal biological treatments. Failure to obtain a normal degree of treatment generally is due to overloading either with respect to volume or organic matter, or both. Occasionally, impaired efficiencies may be traced to the development of septic conditions in sewer lines or to excessive amounts of insoluble solids giving rise to difficulties in primary sedimentation tanks and sludge digestors. The first can be corrected by the addition of lime, soda ash, or by chlorination prior to admittance of the waste to the sewer system, and the latter by efficient screening at the processing plant.

The activated sludge municipal treatment plant at Celina, Ohio, was designed to receive industrial wastes, the largest contributor being a canning plant packing a variety of vegetables.^{41,42} The population equivalents of the combined wastes for the years 1942 and 1943 were 15,000 and 11,800 respectively, of which 5,000 was contributed by the town population. Chemicals are used to aid in the removal of suspended solids and BOD in the primary settling tanks to reduce the load in the aeration basins. Chemical treatment is required only when the cannery is in operation or when the creamery disposes of sour skim milk. The Celina plant has consistently maintained a high degree of treatment. The over-all BOD reduction for the month of September, 1943, is reported as 98.4 per cent, during which time the cannery operated a total of 387 hours on beets, tomatoes and potatoes. A summary of some of the operating data is given in Table 5. The total direct charge to industry is \$2,400 per year of which \$2,000 is contributed by the cannery. The total operating costs for 1942 and 1943 were \$7.30 and \$9.00 respectively per 1,000 pounds of BOD removed. The actual net cost to the town was \$0.87 per capita for 1942 and \$0.83 for 1943.

Pretreatment by chemical precipitation prior to discharge to a municipal treatment plant is sometimes necessary. The Cedarburg, Wisconsin, municipal plant consists of primary settling, rock filtration, secondary settling, and sand filtration. Table 6 presents data collected during periods when this municipal plant received either no cannery waste, chemically pretreated pea cannery waste, or beet cannery waste.⁴⁶ Despite the fact that this plant was somewhat overloaded by domestic sewage alone, as shown by a BOD reduction of only 77 per cent, exclusive of sand filtration, it was able to handle a heavy loading of chemically pretreated cannery wastes. The final plant effluents were water-clear, odorless and stable, although the conversion of nitrogen to nitrites or nitrates was negligible.

Published reports available on the treatment of canning plant wastes at other municipal sewage plants discuss individual problems involved.^{10,13,18,20,22,26,33,36,45,46,49,50}

TABLE 5. ACTIVATED SLUDGE TREATMENT PLANT, CELINA, OHIO

Month	Avg. Daily Flow (gal)	Susp. Solids		5-Day BOD			D.O. Final (ppm)	pH		Ind. Wastes		Chemicals Used	
				Raw	Final	Reduction (%)		Raw	Final	Canning (hrs)	Milk (tons)	Lime (tons)	Iron (tons)
		Raw	Final										
Jan.	627,000	367	11	357	11.0	97.0	5.5	5.9	7.2				0.03
Feb.	648,000	269	10	362	10.7	96.1	4.5	6.3	7.3				
March	877,000	205	16	386	17.0	91.7	5.4	5.5	7.1				
April	664,000	255	10	427	8.9	96.5	4.9	6.4	7.2		6.5	0.12	0.06
May	1,418,000	200	19	382	11.1	94.5	4.3	6.3	7.2		41.5		
June	696,000	330	9	482	8.8	97.3	4.6	5.8	7.2	113	31.5	1.88	0.51
July	707,000	357	13	439	9.0	97.5	4.4	5.6	7.2	171	3.5	3.60	1.37
Aug.	793,000	352	9	414	5.9	98.3	4.6	5.3	7.3	249	1.0	4.83	1.65
Sept.	586,000	380	12	395	6.1	98.4	4.9	5.0	7.4	387	3.0	7.77	2.89
Oct.	515,000	371	18	529	7.3	98.4	4.9	6.2	7.1	233		5.37	2.27
Nov.	524,000	445	9	560	12.5	97.2	4.6	5.8	7.2	161		3.35	1.51
Dec.	425,000	269	12	395	10.5	96.1	4.6	6.8	7.1	110		2.28	0.96

TABLE 6. BIOLOGICAL FILTRATION TREATMENT PLANT, CEDARBURG, WISCONSIN

Sample	pH	5-day BOD	BOD Reduction	Solids				Nitrogen			
				Total	Volatile	Suspended		Total	Ammonia	Nitrites	Nitrates
						Total	Volatile				
Domestic Only—Total Volume 220,800 gallons											
Raw	7.0	270		890	410	320	210	15.2	20.4	0.0	0.0
Primary effluent	7.0	240	10	800	360	160	140	12.4	23.2	0.0	0.0
Rock filter effluent	7.1	83	69	740	290	110	92	8.8	3.2	0.6	9.6
Secondary effluent	7.3	62	77	750	320	80	64	4.8	2.8	0.6	20.0
Sand filter effluent	7.4	18	93	740	350	20	16	0.8	0.4	0.03	36.0
Domestic and Pea Canning Wastes—Total Volume 561,000 gallons											
Raw	6.0	610		1,380	660	110	96	27.6	17.6	0.0	0.0
Primary effluent	6.0	570	7	1,330	740	88	78	24.4	17.6	0.0	0.0
Rock filter effluent	6.8	240	61	1,040	340	70	50	12.0	11.2	0.0	0.0
Secondary effluent	6.8	230	62	1,030	410	64	36	10.8	12.0	0.0	0.0
Sand filter effluent	7.3	49	92	910	220	30	14	6.0	3.2	0.08	1.2
Domestic and Beet Canning Wastes—Total Volume 412,000 gallons											
Raw	6.8	360		1,410	800	160	110	15.6	9.2	0.0	0.0
Primary effluent	6.8	340	7	1,070	540	130	100	15.8	12.4	0.0	0.0
Rock filter effluent	7.5	60	83	870	290	68	48	8.4	12.4	0.0	0.0
Secondary effluent	7.7	56	84	730	300	42	30	6.0	3.2	0.0	0.0
Sand filter effluent	7.2	13	96	690	240	10	6	1.6	0.8	0.03	4.0

Irrigation Fields

The most economical method for the disposal of liquid wastes to avoid all stream pollution from food plants is by means of land irrigation or soil absorption. A prerequisite is the availability of a porous soil with a high water absorption capacity. In some areas a high water table prevents utilization of otherwise satisfactory soil. Any application to land whether in the form of absorption areas or impounding lagoons pre-supposes the absence of underground seepage which might contaminate wells, springs or streams.

The several methods of soil absorption consist of direct application to gravel pits, uniform distribution to sandy areas or fields, or discharge into furrows. Odors generally have not been objectionable when care has been observed to prevent local ponding and by rotating the application of wastes to prevent water-logging. If further odor control is necessary, sodium nitrate may be added to the waste before application.

The largest number of irrigation fields for the disposal of cannery wastes are found in Iowa. One field receiving pea and corn wastes has been in operation since 1934. An average flow of 176 gpm is discharged in furrows approximately 24 inches wide at the top, 15 inches wide at the bottom, and 9 inches deep, which distribute the waste over a field 1.88 acres in area. The ridges are 36 inches wide. The soil is a dark loam. Waste from a header ditch is diverted into one of the furrows until it is full, then into a second, and so on. The cycle is repeated when the last furrow has been filled.

Experience with irrigation fields in Iowa has led to the following recommendations:⁷

- "(1) Choose a location where the soils are of such a substance and texture that they will readily absorb the wastes.
- "(2) Construct the furrows with level bottoms to prevent ponding and the development of odors.
- "(3) Do not add wastes to furrows until they have become completely empty.
- "(4) Protect the field from flooding by surface runoff.
- "(5) Provide constant attendance to direct the flow, remove the solids from the bottom of the furrows, and prevent ponding.
- "(6) Permit weeds to grow to utilize transpiration and to reduce wind sweep for odor control.
- "(7) Where a moderately loose soil is available, provide at least one acre for each 100 to 150 thousand gallons per day of corn waste. However, more area should be provided for periods of heavy rainfall and for expansion of the plant. The water loading is considered

to be the control rather than the strength or solids content of the waste applied."

Recently, high volume applications of screened canning wastes have been made successfully on natural wooded areas. High volume applications can not be made on areas where the soil structure has been modified by plowing, artificial fertilization, or other means.

Lagoons

The earliest method of treating cannery wastes appears to have been the use of impounding lagoons. This procedure soon fell into disrepute because of complaints due to offensive odors unless the lagoons were located well away from habitation or highways. Various attempts to con-



FIGURE 8. Cannery waste lagoon

trol odor production through the use of lime, chlorinated lime, sodium hydroxide, oil and disinfectants have been unsuccessful. The use of lagoons up to the present time has been restricted to wastes produced from seasonal operations.

Nitrated-Treated Lagoons. Studies undertaken in 1940 on the addition of sodium nitrate to cannery wastes showed that odors could be completely eliminated or partially suppressed according to the quantity of nitrate added.³⁵ The function of sodium nitrate is three-fold: (1) to furnish available oxygen from the nitrate radical for aerobic bacterial activity during the early stage of decomposition, (2) to stimulate the growth of chlorophyllaceous organisms which in turn produce additional oxygen by photosynthesis at later stages, and (3) to maintain an alkaline reaction through the formation of sodium carbonate.

Fruit and vegetable wastes normally undergo rapid anaerobic decomposition with the production of offensive odors of organic acids, nitrogen

decomposition products and hydrogen sulfide. Sodium nitrate by directly and indirectly supplying a source of oxygen minimizes the formation of odorous compounds. In practice it has not been found economical to completely satisfy the oxygen demand of the waste. Experience with properly operated lagoons has shown that the odors produced are mild in comparison with untreated lagoons. The odors are produced over much shorter periods of time and should not be detectable at distances over 1,000 feet under most unfavorable atmospheric conditions.

An extensive cooperative study of sodium nitrate-treated and untreated lagoons was undertaken by the National Cannery Association and the Wisconsin State Board of Health.⁴⁷ Lagoons treated with sodium nitrate for odor control should be constructed as single lagoons in preference to several small ones operated in series. In the latter case, the first lagoon remains highly septic as it continually receives strong raw waste and does not receive the dilution and other beneficial effects of the wastes contained in the lower lagoons. If topographic features require the construction of more than one lagoon, the flow of waste should be apportioned among the several lagoons.

Lagoons should be of sufficient capacity to receive the entire volume of liquid waste produced in a season. Nitrate-treated lagoons should have sufficient extra capacity to retain approximately 25 per cent of the waste in the lagoon at all times. The retention of a substantial volume of waste in a lagoon is of distinct advantage for the following reasons: (1) immediate dilution of the strong waste admitted to the lagoon at the start of a new pack with a quantity of water saturated with oxygen and containing chlorophyllaceous and other seeding organisms retained from the previous year, and (2) prevention of prolific growth in the lagoon of weeds which, if present, would subsequently decompose adding a considerable load of organic material.

A large shallow lagoon rather than a small deep one is recommended to provide better natural aeration and to take advantage of the stimulating effect of sunlight on biological life within the lagoon on a larger proportion of waste. Economic considerations usually prohibit full utilization of the advantages of shallow lagoons. A maximum waste depth of 5 feet is suggested and a depth of 3 feet recommended.

Lagoons of any type must be located on a site where seepage will not contaminate wells or underground sources of water and must be constructed with watertight embankments. Embankments should have a top width of not less than 7 feet with an inner slope of $2\frac{1}{2}$ horizontal to 1 vertical and an outer slope of 2 to 1 and sufficient freeboard for safety against frost disturbance. The outer slope should be protected from erosion by a cover of grass or native vines. A diaphragm barrier may be re-

quired for protection against muskrats. The lagoon drainage pipe valve must be provided with a lock to prevent opening by unauthorized persons. Wastes are universally discharged into a lagoon at the point requiring the least pipe line. Observations have shown that as a consequence, and especially in large lagoons, the strong wastes are retained at the receiving area. In order to obtain the advantages of mixing it is suggested that the raw waste be admitted at a centrally located point or at intervals along the length of the lagoon.

During the past 5 years most of the new installations for treating cannery wastes have been lagoons treated with sodium nitrate. Excellent BOD reductions have been obtained and no difficulty has been experienced in the discharge of these wastes into small streams following winter storage. The operation of these lagoons is relatively simple, but an understanding of the principles and limitations involved is required for satisfactory performance. Of particular importance are the exclusion of screenable solids and of stack liquors, the retention of waste in the lagoon as previously discussed, and the addition of sodium nitrate in the proper amount every day that wastes are discharged into the lagoon. Commercial agricultural sodium nitrate containing 98 per cent NaNO_3 (54.7 per cent available oxygen) is used. The nitrate may be added from drip tanks or by periodic additions of the solid material to the screened waste at the pump sump at frequent intervals during the operating period. For convenience, dosage rates are expressed in terms of 1,000 cases of No. 2 cans packed. Appropriate correction should be made for cans of other sizes. Typical dosage rates for wastes of average strength are as follows:

Type of waste	Lbs sodium nitrate per 1,000 No. 2 cases
Beans, green or wax	20
Beans, lima	60
Beets	200
Carrots	200
Corn	200
Peas, early	200
Peas, late	150
Tomatoes	200

The indicated rates may be reduced by as much as 50 per cent when the wastes are admitted into a lagoon containing a substantial amount of nitrate-treated waste other than the 25 per cent carry-over from the previous season. Adjustments must, of course, be made for wastes deviating substantially from average strengths.

A set of results obtained on the nitrate treatment of lagooned pea and corn wastes are shown in Figure 9. This lagoon was a small one, 1.4 acres,

having a capacity of 2,700,000 gallons. Some waste was present in the lagoon prior to the pea canning season which started on June 25 and ended on July 20. An average of only 142.5 pounds of sodium nitrate per 1,000 cases of No. 2 cans packed was used during this period. The corn pack started on August 17 and ended on September 21. The average nitrate dosage for the corn pack was 104.5 pounds per 1,000 cases. The BOD of the lagooned pea waste on the day prior to the corn pack was 156 ppm and the pH 8.6. The maximum BOD in the lagoon during the corn pack

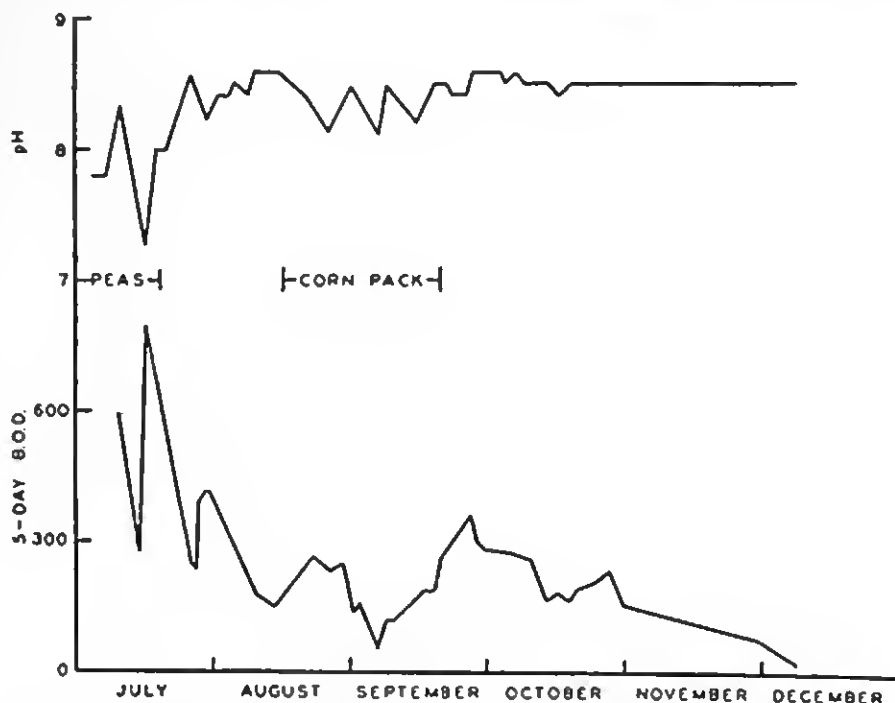


FIGURE 9. Results of lagooned sodium nitrate-treated pea and corn wastes

was 384 ppm although the screened raw corn waste was found to average 3,180 ppm during the early part of the pack. By December 9, the BOD was 23 ppm and the pH 8.4. The maximum distance to which odors were noted during numerous periods of observation was 50 feet from the lagoon. The performance of this lagoon from the standpoint of odor control over a period of several years has been consistent. The presence of diluting and seeding material, better than average mixing, and faithful nitrate treatment are known contributing factors. Experience with this same lagoon prior to nitrate treatment resulted in numerous odor complaints. Reference should be made to National Cannery Bulletin No. 29-L⁴⁷ for data on other lagoons and for a more complete discussion. Black⁶ and Ryan³⁴ have also reported on the operation of sodium nitrate-treated lagoons.

Untreated Lagoons. Lagoons which can be located in isolated sites where odor will not lead to complaints are in use. The special features of con-

struction and operation of nitrate-treated lagoons do not apply to isolated lagoons. Screening, however, will prevent the deposition of solids eventually requiring removal. Some wastes in untreated lagoons do not undergo as complete oxidation as is obtained in nitrate-treated lagoons. Provision must be made for the final disposal of the relatively strong liquid remaining in untreated lagoons by soil absorption or adequate stream dilution at times of high-stream flow. Some reduction in the strength of lagooned wastes occurs where climatic conditions permit freezing.^{32,47}

Limited observations and private communications indicate that deep lagoons receiving tomato wastes, including all solids, have operated satisfactorily provided the liquid portion can be disposed of prior to the following packing season. Lagoons of this type which have been in operation for several years become substantially sealed at the surface with a thick layer of digested solids. These lagoons are in effect anaerobic digesters.

ENSILAGE STACK LIQUOR

The seepage liquor from pea vines and corn cobs and husks constitutes a disposal problem at many canning and freezing plants. The liquor is heavily laden with soluble organic matter produced during the fermentation curing process. The liquor as it leaves the stack has an obnoxious odor of butyric acid and organic nitrogen decomposition products.

Eldridge¹⁶ reports pea stack liquor seepage of 1.5 to 5.0 gallons per case of No. 2 cans packed, depending on the amount of rainfall during the storage period. The succulency of the vines is also an important consideration. From 20,000 to 30,000 gallons of seepage has been obtained from pea vines from one hundred acres. Baker⁴ reported a flow of 1,000 to 1,500 gallons per day from the pea vines from 100 acres during the period of maximum flow. During a relatively dry season, 1.65 gallons of pea stack liquor was produced per No. 2 case of peas packed.³⁰ Halvorson²¹ reports a flow of 15,000 to 75,000 gallons per day of corn stack liquor, depending upon the amount of water carried into the stack, from the production of 5,000 cases of No. 2 cans per day.

An indication of the characteristics of pea stack juice can be obtained from the following data:⁴⁶

pH		3.6
5-day BOD	ppm	78,000
Solids:		
Total	ppm	71,800
Total volatile	ppm	57,740
Soluble	ppm	70,380
Suspended	ppm	1,420
Suspended volatile	ppm	1,140

The above pea liquor came from a covered silo. Other workers have reported 5-day BOD values ranging from 35,000 to 57,000 ppm on wastes presumably from open stacks. The 5-day BOD of corn stack liquor has been reported as 22,000 to 40,000 ppm and lima bean stack liquor as 25,000 ppm.

Experimental efforts to treat pea stack liquor chemically with lime alone, or in combination with iron salts, have not yielded satisfactory results on either raw or diluted liquor. Large reductions have been obtained percentage-wise but the remaining BOD of unprecipitated constituents was excessive. It does not appear to be economically advisable to treat stack liquor by chemical coagulation.

Stacks located at factory sites should be provided with a concrete base and gutters protected against entrance of ground run-off water. Stack drainage should be piped by gravity flow to an underground covered tank. Two methods of final disposal are in general use. The liquor may be hauled away periodically in tank wagons and disposed of by soil absorption in isolated areas. Storage tanks capable of holding the entire volume of stack liquor permit discharge of the liquor at very slow rates at times of high stream flows. Stack liquor should never be discharged with other factory wastes to a municipal treating plant or to impounding lagoons treated with sodium nitrate for odor control. Isolated lagoons or irrigation fields whose odors do not create objections may receive stack liquor, but such addition will create additional odor hazard.

Open stacks give rise to atmospheric pollution, particularly the large stacks located at factories. They also attract and breed insects and harbor rodents. The present trend is to remove vining operations from the factory site and locate a number of small stations throughout the growing area. Seepage from small stacks can be taken care of by soil absorption. Frequent dusting of the outer portions of the stack with lime or commercial deodorants will reduce atmospheric pollution.

Costs

Estimates on the cost of construction and operation of cannery treatment plants as given in published reports are all based upon prewar cost data. No uniform method of cost presentation has been adopted. The advent of high-speed closing machines, the use of hydraulic methods of conveying products and other factors have greatly altered typical rates of production, volumes and strengths of wastes. Cost estimates based upon a "two-line factory" in an industry which always has been characterized by a great lack of uniformity in waste production should be used with caution.

Cost estimates³⁰ based upon pea and tomato waste flows of 100,000 gallons per 12-hour working day are as follows:

- (a) Screening. Cost of unit \$1,200. Total cost of operation including cost of disposal of screenings, \$10 per day.
- (b) Chemical treatment. Cost of plant construction \$5,000. Total operating cost including labor, chemicals, interest on investment and depreciation \$30 per day.
- (c) Trickling filters. Cost of plant operated at 2.0 mgad without providing for sedimentation but including screening, \$6,000. A plant operating at 0.5 mgad was estimated to cost \$20,000. Total operating cost estimated at \$25 and \$35 per day, respectively.

On the same basis Wisconsin studies⁴⁶ indicate a similar cost for chemical treatment, while a high-rate filter (20 mgad) with secondary sedimentation and recirculation would cost about \$15,000 for plant construction and \$35 per day total operating expenses.

The cost of chemical and biological treatments is high when considered in the light of the quality of effluent produced. A 50 per cent reduction by chemical treatment and 50 to 85 per cent by biological filters on wastes having initial BOD's of several thousand parts per million leaves an effluent higher in pollutorial value than raw domestic sewage. A complete biological treatment plant capable of reducing vegetable or fruit wastes with high initial BOD's to a final effluent comparable to that obtainable from domestic sewage (as required by some state agencies) would, if constructed and operated by packers, be prohibitive in cost.

Disposal by irrigation fields, where practical, provides an inexpensive method of treatment.⁴⁷ At one plant wastes were discharged at an average rate of 176 gpm during the hours of work and clean-up. The total operating cost for the disposal of unscreened wastes, including the cost of leasing the land, was \$280. This amounted to 0.12 cents per case. At another plant having an average flow of 123 gpm the cost, exclusive of screening, was 0.097 cents per case. No information was obtained on the cost of piping and construction of irrigation furrows.

The estimated cost of construction of a lagoon⁴⁷ capable of handling 10 million gallons of waste from the canning of 200,000 cases of No. 2 cans each of peas and corn (assuming 25 gallons per case) with one-fourth additional capacity for wastes retained in the lagoon, the maximum waste depth to be 3 feet, freeboard 3 feet, top embankment width 10 feet, with an inner slope of 2.5 to 1 and outer slope of 2 to 1 would be as follows:

Items	Cost
Land: 15.0 acres at \$100 per acre	\$1,500.00
Pump sump and pumping facilities	650.00
Pipe line: 1,000 feet	1,000.00
Construction of lagoon and installation of facilities	5,000.00
TOTAL COST	\$8,150.00

The cost of operation of the lagoon was figured as follows:

Items	Cost
Labor: 800 hours at \$0.60	\$480.00
Pumping	40.00
Taxes at \$2.00 per acre	30.00
Interest on investment at 3 per cent	<u>245.00</u>
TOTAL COST OF LAGOONING	\$795.00

If treatment for odor control was desired, using sodium nitrate at \$36 per ton delivered and assuming wastes of average strength, the additional cost was estimated as follows:

Product		Dosage rate per 1,000 No. 2 cases lbs	Sodium nitrate required lbs	Cost per No. 2 case cents
Early peas	100,000	200	20,000	0.36
Late peas	100,000	150	15,000	0.27
Corn	<u>200,000</u>	<u>100</u>	<u>20,000</u>	<u>0.18</u>
TOTAL	400,000		55,000	0.25

On a per case basis, and exclusive of screening, the cost of lagooning without sodium nitrate treatment would be 0.20 cents per case and 0.45 cents per case with sodium nitrate treatment.

WASTE UTILIZATION

Canning, freezing and dehydration plants produce two types of waste; liquids and solids. Liquid wastes after screening carry a total organic content of only a few tenths of one per cent consisting for the most part of carbohydrates in suspension and solution. Such low concentrations offer no possibility of utilization. A few liquid wastes such as blancher waters containing 2 or 3 per cent of organic material are produced in quantities insufficient to warrant consideration. It is not practical, as in some industrial processes, to reuse water in a closed system. Owing to the nature of the products involved, use of fresh water or frequent change of water is required to secure thorough washing of foods and to prevent build-up of bacterial contamination. To a limited extent, and with certain products, water may be used for counter-flow washing. Can cooling water is sometimes reused for cooling or in preliminary washing operations. The reuse of water is generally avoided unless water conservation is necessary.

Utilization of solid wastes from fruit and vegetable canning plants has been reviewed by Wiegand⁴⁸ and Sanborn.³⁷ Theoretically, large quantities of usable by-products could be obtained. Utilization has not been practiced more extensively owing to: (1) the seasonal nature of fruits and vegetables; (2) the perishable nature of the wastes which require immediate conversion; (3) insufficient tonnage of waste produced at most

plants to justify economical conversion; (4) reluctance to assume additional responsibilities during intensive packing seasons; and (5) the prospect of comparatively small financial return, since the by-products produced would enter highly competitive markets. Most of these objections could be met by the establishment of separate waste utilization plants centrally located within economic hauling distances from several processing plants and operated in conjunction with other agricultural products.

Solid waste materials available at canning plants are listed in Table 7 for the more important vegetable and fruit products producing sizable quantities of waste under normal operating conditions.

TABLE 7. SOLID WASTES FROM CANNING PLANTS

Product	Farm weight as received (tons)	Average waste		Predominant type of waste
		(tons)	(%)	
Vegetables				
Asparagus	76,000	31,000	41	butts
Beans, green	298,000	36,000	12	snips, culls
Beans, lima	182,400	155,000	85	vines
Beets	186,000	46,500	25	trimmings
Cabbage	107,600	27,000	25	trimmings
Carrots	43,400	27,000	33	trimmings
Corn	1,162,000	1,000,000	86	husks, cobs
Peas	1,751,000	1,385,000	79	vines
Spinach	92,400	37,000	40	trimmings
Tomatoes	2,659,000	665,000	25	skins, cores, culls
Fruits				
Apples	200,000	70,000	35	peels, cores
Apricots	142,000	36,000	25	pits
Cherries, sour	60,800	10,000	15	pits
Grapefruit	1,233,000	710,000	58	peels, pulp, seeds
Peaches	401,600	160,000	40	pits
Pears	249,700	105,000	42	peels, cores

The only vegetable wastes utilized in quantity are pea vines and corn husks and cobs which are stored for winter animal feeding. During curing, approximately 30 per cent weight is lost, partly in the outer portion of stacked ensilage which becomes unsuitable for feeding and partly in ensilage juice, rich in soluble organic material. Artificial drying would permit conservation of these losses. Investigations on dehydrated pea vines and other agricultural wastes have shown these to be valuable feeds with high carotene and other vitamin content.^{9,29,40} The first commercially dried pea and corn feeds were prepared by a canner who dried these wastes in season along with alfalfa and soy bean foliage.¹

No published reports are available concerning the operation and eco-

nomies of several cannery operated tomato drying plants. Templeton³⁹ has reported on pilot plant drying of tomato waste. Some of the remaining vegetable wastes are utilized to a minor extent for feed in the wet state or returned to land for soil enrichment. The Western Regional Research Laboratory of the U.S. Department of Agriculture and the College of Agriculture of the University of California have investigated the possibilities of utilizing asparagus butts for feeds, fertilizers and fiberboard, and the vacuum concentration of expressed butt juice for penicillin mold culture. While special by-products of economic importance may be forthcoming, utilization of vegetable wastes will, in all probability, await the development of more economical driers for animal feed production.

Fruit wastes offer a wide variety of by-products, some of which are established commercially. Vinegar, pectin and syrup are obtained from apple wastes. Edible sweet oil and bitter almond oil are produced from apricot and peach pits. Kester and Van Atta²⁷ have reported on the properties and production of pit and seed oils. The production of feed yeast from pear waste is under investigation by the Western Regional Research Laboratory¹⁷ and from citrus press juice by the U.S. Citrus Products Laboratory.⁸⁵

The recovery of by-products from the citrus industry has been the subject of numerous investigations particularly with reference to grapefruit wastes.⁸⁴ Citrus by-product plants are in operation by canners and as individual enterprises. Dried citrus meal for animal feeds is the principal waste recovery product. Molasses, pectin, alcohol, and peel and seed oils are also recovered in commercial quantities.

Feed meal is obtained from citrus refuse containing peel, pulp and seeds. The waste is ground with lime and the mixture cured in bins or pug mills. Treatment with lime reduces the acidity and reacts with pectin constituents. The latter serves two purposes: (1) facilitate partial dewatering in presses, if desired, and (2) prevent sticking to hot surfaces during drying. Molasses is obtained from the juice expressed from the citrus lime mixture by evaporation in triple- or quadruple-effect evaporators. At plants where molasses is recovered, the disposal of a potent liquid waste has been solved. Figure 10 presents a flow chart of citrus waste recovery by two methods, together with the yields of feed and molasses from the wastes obtained from 1,000 boxes of grapefruit incident to the canning of the juice. One large canner recovers 65 tons of meal and 30 tons of molasses daily during peak operations.

Commercial recovery of edible sugar syrup from citrus and pineapple wastes by the ion exchange process is a new development.³ Pineapple waste consisting of shell, trimmings and rejected fruit is dejuiced in screw presses, the pulp being dried and sold for cattle feed. The juice is screened

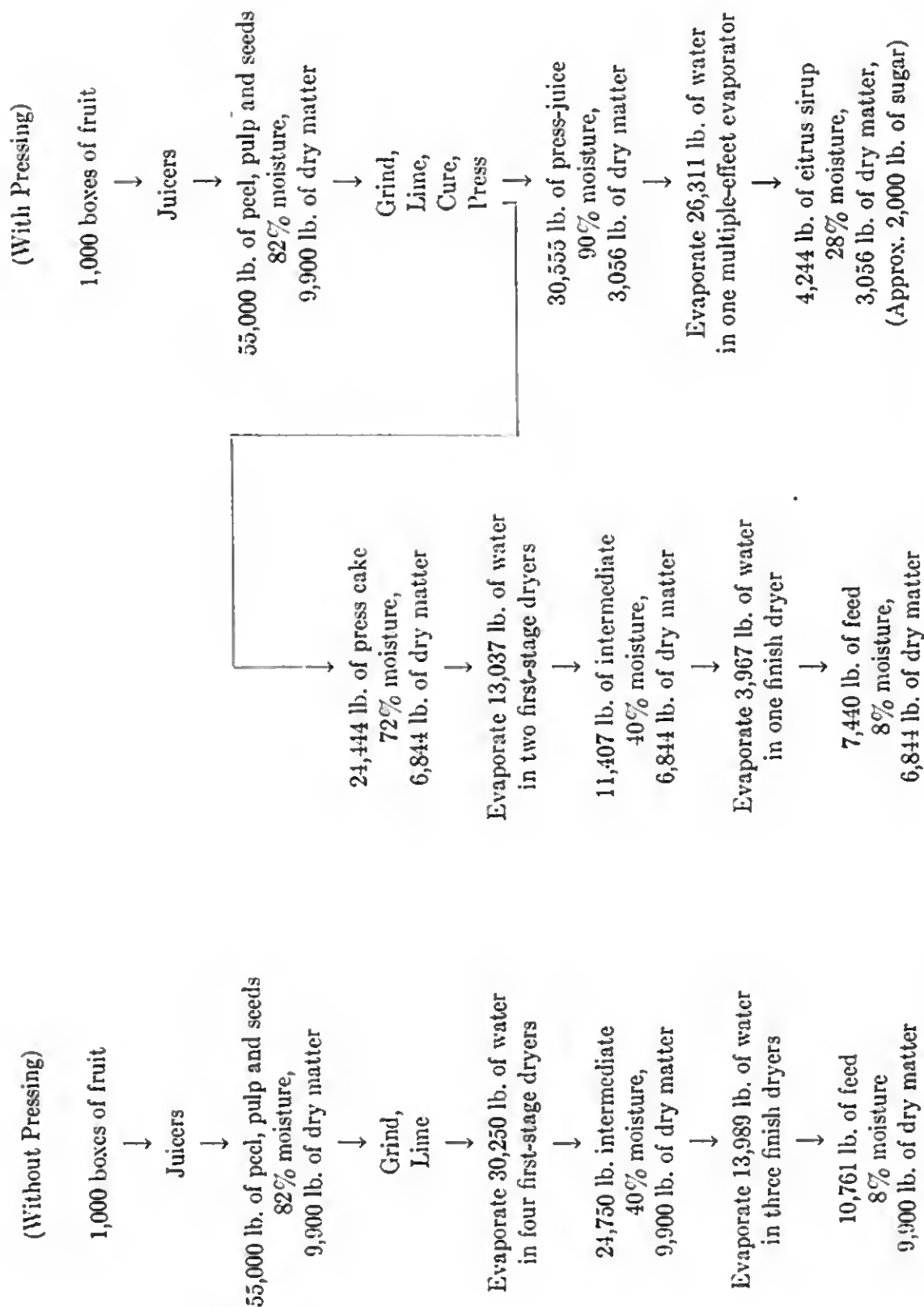
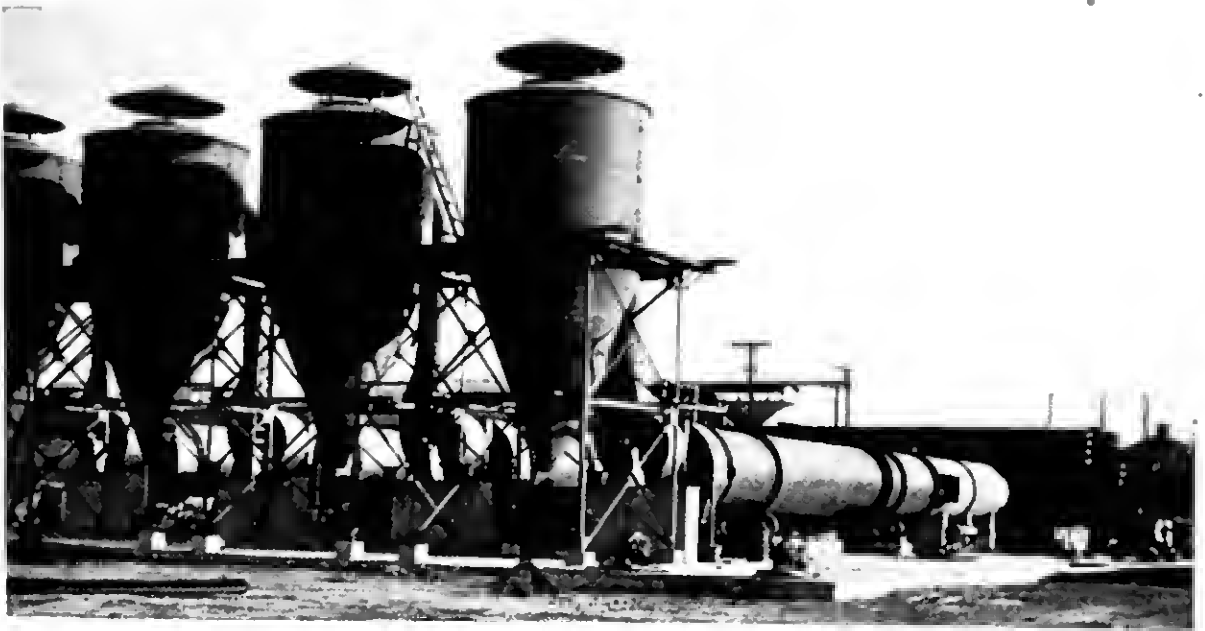


FIGURE 10. Hourly performance flow-chart of citrus feed manufacture (64)



(Courtesy Texan Citrus Exchange)

FIGURE 11. Citrus feed dehydrating plant during construction, showing rotary driers and cyclone hoppers



(Courtesy Hawaiian Pineapple Company, Limited)

FIGURE 12. Sugar recovery from pineapple waste. Part of a battery of ten ion exchange cells during installation

to remove the coarser insoluble material, heated to precipitate albumin, treated with Filteraid, and filtered to yield a clear liquid. The juice is limed to a pH of 5.2 and heated in order to precipitate calcium citrate which is separated by filtration. The juice is cooled and passed through ion exchange units to remove ash, organic acids and colored impurities. The purified solution is then concentrated in a quadruple-effect evaporator to a syrup of about 30 per cent sugar. The syrup is adjusted to the desired sugar content for use with canned pineapple. The calcium citrate cake is washed with hot water, treated with sulfuric acid, calcium sulfate then being removed by filtration. The crude citric acid liquor is concentrated and crystallized to yield an impure acid which is further purified and recrystallized to yield U.S.P. citric acid.

Large quantities of fruit and vegetable wastes remain to be disposed of as garbage. Discovery of new by-products, development of markets for known by-products and technological advances in recovery methods, are needed to convert these wastes into products which will at least substantially reduce the present cost of disposal and perhaps yield some net financial return.

References

1. Anon., "Dehydrating canning waste," *Food Packer*, 28, No. 7, 40 (1947).
2. Anon., "How to treat wastes," *Food Industries*, 9, 440 (1937).
3. Anon., "Ion exchange plant recovers sugar from fruit waste," *Food Industries*, 18, 1846 (1946).
4. Baker, C. M., "Pea canning waste disposal," *Canning Age*, 6, 895 (1925).
5. Baker, C. M., Warrick, L. F., and Smith, J. P., "Treatment of pea canning wastes," *Wisconsin State Board of Health Bull.* (1926).
6. Black, H. H., "Treating corn cannery wastes," *Canning Age*, 23, 325 (1942).
7. Bolton, P., "Cannery waste disposal by field irrigation," *Food Packer*, 28, No. 9, 42 (1947).
8. Citrus waste by-products (recent references)
 - (a) Arnold, P. T. D., Becker, R. B., and Neal, W. N., "The feeding value and nutritive properties of citrus by-products," *Fla. Agr. Expt. Sta. Bull.*, 354 (1941).
 - (b) Atkins, C. D., Wiederhold, E., and Moore, E. L., "Vitamin C content of processing residues from Florida citrus fruits," *Fruit Products J.*, 24, 260 (1945).
 - (c) Hall, H. W., "Disposal of citrus wastes," *Civil Eng.*, 14, 15 (1944).
 - (d) Heid, J. L., "Drying citrus canning wastes and disposing of effluents," *Food Industries*, 17, 1479 (1945).
 - (e) Nolte, A. J., von Loesecke, H. W., and Pulley, G. N., "Feed yeast and industrial alcohol from citrus-waste press juice," *Ind. Eng. Chem.*, 34, 670 (1942).
 - (f) Pulley, G. N., Moore, E. L., and Atkins, C. D., "Grapefruit-cannery wastes yields crude citrus pectin," *Food Industries*, 16, 285 (1944).

- (g) Veldhuis, M. K., and Gordon, W. D., "Experiments on production of feed yeast from citrus press liquor," *Citrus Industry*, 7 (Jan. 1948).
- (h) Weber, G. L., "Plastics from citrus wastes," *Pacific Plastics Mag.*, 1, No 4-5, 5-6, 44, 46 (1943).
9. Colker, D. A., and Eskew, R. K., "Processing vegetable wastes for high-protein, high-vitamin leaf meals," Eastern Regional Research Laboratory, *Bur. Agr. Ind. Chem. Circ. A1C-76* (1945).
 10. Crist, M. L., "Industrial wastes: Sewage = 4:1," *Sewage Works Eng.*, 18, 207 (1947).
 11. De Martini, F. E., Moore, W. A., and Terhoeven, G. E., "Food dehydration wastes," *U.S. Pub. Health Rept., Suppl. No. 191* (1946).
 12. Dickinson, D., "Purification of wastes from fruit and vegetable canneries," *The Surveyor*, 106, 1001 (1946).
 13. East, C. A., "Modern sewage treatment plant at Vernon, B. C.," *Eng. and Contract Record*, 53, No. 43, 11 (1940).
 14. Eldridge, E. F., "Experience with special cannery wastes—beets, tomatoes and squash," *Mich. State Coll. Eng. Expt. Sta. Bull. No. 78* (1938).
 15. Eldridge, E. F., "The treatment of red beet, tomato and squash cannery wastes," *Mich. State Coll. Eng. Expt. Sta. Bull. No. 83* (1938).
 16. Eldridge, E. F., "Symposium on industrial wastes—canning industry," *Ind. Eng. Chem.*, 39, 619 (1947).
 17. Feustel, I. C., and Thompson, J. H., "Pear canning waste may be valuable for yeast culture," *Western Canner and Packer*, 38, No. 4, 60 (1946).
 18. Furphy, H. G., and Ley, J. B., "Country Town Sewage: Installation at Shepparton, Vic., treating canning factory waste," *Commonwealth Eng.*, 25, 413 (1938).
 19. Gray, H. F., and Ludwig, H. F., "Characteristics and treatment of potato dehydration wastes," *Sewage Works J.*, 15, 71 (1943).
 20. Gregory, T. R., and Kimball, J. H., "Cannery wastes at Palo Alto," *Sewage Works J.*, 9, 607 (1937).
 21. Halvorson, H. O., Johnson, D. W., and Tsuchiya, H., "Treatment of corn canning wastes," *Canner*, 90, No. 7, 12; No. 8, 12 (1940).
 22. Hert, O. H., "Tomato canning plant wastes," *Food Packer*, 28, No. 10, 40 (1947).
 23. Holmes, J. A., and Fink, G. J., "Sodium aluminate as a coagulant in chemical treatment of cannery waste waters," *Ind. Eng. Chem.*, 21, 150 (1929).
 24. Illinois Water Survey Series No. 11, "The investigations on the disposal of canning factory wastes at Washington, Ill." (1913).
 25. Jones, E. E., "Disposal of waste waters from the preparation of vegetables for drying," *J. Soc. Chem. Ind.*, 64, 80 (1945).
 26. Kennedy, C. C., "Improvements in sewage treatment at Stockton, Calif. as effected by cannery operations," *Sewage Works J.*, 9, 271 (1937).
 27. Kester, E. B., and Van Atta, G. R., "Minor oil-producing crops of the United States," *Oil and Soap*, 19, 119 (1942).
 28. Michigan Dept. of Health, Water Pollution Control, *Cannery Wastes, Bull.*, (Apr. 1927).
 29. Morris, R. H., Colker, D. A., and Chernoff, M. F., "Vegetable wastes, availability and utilization," Eastern Regional Research Laboratory, *Bur. Agr. Ind. Eng., Circ. A1C-51* (1944).
 30. New York State Board of Health, "The treatment of canning wastes" (1930).
 31. Ohio Dept. of Health, "Progress report on cannery waste treatment studies." (Undated and un-numbered. Studies conducted in 1926 and 1927.)

32. Riedesel, P. W., and Lawson, W. R., "Freezing as a factor in the stabilization of corn-cannery wastes," *Sewage Works J.*, **17**, 952 (1945).
33. Ryan, W. A., "Effect of cannery wastes on operation of sewage treatment plants," Discussion by Bernhardt, C. J., *Sewage Works J.*, **12**, 99 (1940).
34. Ryan, W. A., "Experience with sodium nitrate treatment of cannery wastes," *Sewage Works J.*, **17**, 1227 (1945).
35. Sanborn, N. H., "Nitrate treatment of cannery wastes," *The Canner*, **92**, No. 16, 12 (1941).
36. Sanborn, N. H., "Treatment of vegetable cannery wastes," *Ind. Eng. Chem.*, **34**, 911 (1942).
37. Sanborn, N. H., "Food canning waste utilization," *Proc. First Ind. Waste Util Conf.*, Purdue Univ. (1944).
38. Texas State Dept. Health, Bur. Sanitary Eng., "Treatment of wastes from citrus juice canning plants" (1940).
39. Templeton, C. W., "Cost studies on dehydrating tomato wastes," *Food Packer*, **28**, No. 12, 53 (1947).
40. Tomhave, A. E., and Hoffman, E., "A preliminary investigation on the use of certain dried vegetable wastes as poultry feeds," *Univ. Del. Agr. Expt. Sta., Bull.* **247** (1944).
41. Uhlman, P. A., "Three years' treatment of sewage at Celina, Ohio," *Public Works*, **74**, No. 3, 13 (1943).
42. Uhlman, P. A., "Charges to industries for treating their wastes in a municipal plant," *Public Works*, **75**, No. 12, 23 (1944).
43. U.S. Public Health Bull. No. 118, "The purification of tomato canning factory wastes" (1921).
44. von Loesecke, H. W., Pulley, G. N., Nolte, A. J., and Gorseline, H. E., "Experimental treatment of citrus-canning effluent in Florida," *Sewage Works J.*, **13**, 115 (1941).
45. Warrick, L. F., and Beatty, E. J., "The treatment of industrial wastes in connection with domestic sewage," *Sewage Works J.*, **8**, 122 (1936).
46. Warrick, L. F., McKee, F. J., Wirth, H. E., and Sanborn, N. H., "Methods of treating cannery waste," *National Cannery Assoc. Bull. No. 28-L* (1939).
47. Warrick, L. F., Wisniewski, T. F., and Sanborn, N. H., "Cannery waste disposal lagoons," *National Cannery Assoc. Bull. No. 29-L* (1945).
48. Wiegand, E. H., "Dollars from factory wastes," *The Canner*, **98**, No. 10, 12; No. 11, 20 (1944).
49. Wolman, A., and Hall, G. L., Maryland State Dept. Health Ann., "Rept. Bur. San. Eng.," p. 216 (1938).
50. Young, C. H., "Treatment of cherry waste waters," *Public Works*, **74**, No. 11, 25 (1943).

5. Slaughterhouse and Meat Packing Wastes

Willem Rudolfs

Department of Sanitation, Rutgers University, New Brunswick, N.J.

Slaughterhouses—establishments for the killing of animals and the dressing of meat—in the majority of cases are small in size and process relatively little meat or by-products, although in the packing centers the large plants may kill hundreds of animals a day. The packing house industry is more concentrated in the larger cities.

The wastes from slaughterhouses and packing houses are similar chemically to domestic sewage, but are considerably more concentrated. They are almost wholly organic, chiefly dissolved and suspended material. The principal deleterious effect of their wastes on streams and water courses is their deoxygenation.

Stockyard wastes contain animal excreta, fibrous material such as hay and other feeds, and grit. The amount and strength of the waste vary considerably, depending upon whether the pens are covered, the presence or absence of catch basins, practice in manure removal, frequency of flushing, and rainfall. The killing and dressing of meat in slaughterhouse and packing plants produce blood, grease, hair, manure, fleshings and dirt.

Processes

Slaughterhouse. The slaughterhouse is principally a place for killing and dressing with little processing of meat. The process consists of sticking and bleeding the animals on the killing floor. Hides, skins, and pelts are removed from cattle, calves and sheep. Hog carcasses are immersed in scalding water after which the hair is removed by scraping. The insides are removed and some portions sent to the chilling rooms and later sold fresh. Carcasses are trimmed, washed, dried and hung in cooling rooms. Hides are salted and stocked until shipped to tanners or wool processing plants. The segregation of various offal for collection and processing by speciality plants, such as glue and gelatine works, sausage manufacture, and rendering plants, is part of the slaughterhouse operation. Many

slaughterhouses are equipped for rendering inedible greases and fertilizer tankage production.

Packing House. Packing house floor operations are generally carried out with more attention to the recovery of soluble products. Blood is collected, coagulated and dried for edible and inedible uses. The treatment of carcasses is much the same as in slaughterhouses, except that the packing houses process more of the meat by cooking, curing, smoking, pickling, and canning of specialties. The large factories either produce soaps and fertilizers from inedible grease and offal or ship these and tallow, hides, wool, hog hair and glue stocks to subsidiaries or speciality houses.

Raw Materials and Products

The average weight in pounds of animals slaughtered in the United States varies with a tendency toward producing heavier animals according to the Livestock Branch of the United States Department of Agriculture (Table 1).

TABLE 1

Year	Cattle	Calves	Hogs	Sheep or Lambs
1930	956	175	231	82
1935	910	189	227	84
1940	940	191	233	86
1945	948	214	265	94

The annual kill of meat animals in the United States under Federal inspection, which constitutes about 65 per cent of the total estimated kill, expressed in millions of pounds a year and tons per day is illustrated by the figures in Table 2.

TABLE 2

Year	Mil. Lbs	Tons/day	Total Kill
1930	20,223	33,700	67.0
1935	17,262	28,800	63.1
1940	23,410	39,000	65.6
1945	28,117	46,900	64.5

The chief products of slaughterhouse and meat packing plants are the edible portions of the carcasses. By-products of the slaughterhouse consist of hides, skins, pelts, inedible tallows, fertilizer, tankages, offal, pen and paunch manures. Packing house by-products are more numerous. They include hides, skins, pelts, bone and bone products, tallows, glue stocks, bone meal, manufacturing stock (buttons, handles), horns (ornaments, combs), hoofs (buttons, fertilizer, neatsfoot oil, stearine, candles, glue), bristles, hair, sausage casings, tennis and musical strings, surgical ligatures, oxgall, fats (oleomargarine, stearic acid, lubricants, ointments,

soap stocks), meat scrap and blood (fertilizer or feeds), and glands (medicinal preparations).

The approximate percentage yields of meat products and by-products have been estimated²⁵ in Table 3.

TABLE 3

Classification	Percentage of Live Weight			
	Beef	Veal	Pork	Lamb
Edible	60.1	58.9	75.8	53.9
Inedible	10.3	10.1	3.7	17.6
Shrinkage*	29.6	31.0	20.5	28.5

*Evaporation and valueless material.

Sources and Quantities of Wastes

Nearly every operation from the stockyard through the slaughterhouse and packing house is a source of waste liquors and wash waters. All these wastes are highly putrescible, become septic quickly, have a high oxygen demand and a disagreeable odor.

The type of waste produced by the separate operations are shown in Table 4.

TABLE 4

Source	Waste
Stockyard	manure
Killing floor	blood
Dehairing	hair and dirt
Insides removal	paunch manure and liquor
Rendering	stick liquor or press liquor
Carcase dressing	flesh, grease, blood, manure
By-products	grease, offal

Information on the volumes of waste produced from separate operations is limited. The volumes vary greatly; data obtained over many years in Chicago¹⁶ show that water consumption per ton of kill varied from 1,900 to 8,700 gals per 24 hours, averaging 4,130 gals. A survey conducted in Texas²⁴ showed that packing plants that purchased water used considerably less than those owning a water supply. The average use was 220 gals per animal, but the variations were from 75 to 635 gals per equivalent animal. The volume of waste per animal also varies with the degree of processing. Results of the Ohio River Survey²⁵ showed combined raw wastes to be as indicated in the following paragraphs.

Stockyards. Waste from a 27-acre section of the Chicago stockyards for a 12-hour day flow was 23,070 gals per acre.

Slaughterhouse. The volumes of waste are small as compared with those of packing houses, because the uses of water are relatively few and con-

fined largely to carcass washing and for general clean-up. Unit volumes (Table 5) were:

TABLE 5

Number plants	Process	Gals Water per Annual	Hog unit
3	general slaughter	359	156
6	cattle slaughter	395	157
2	hog killing	143	143

Paeking house. Table 6 shows the average combined wastes volumes of different types of paeking houses produced in gallons each 24 hours:

TABLE 6

Number of plants	Type kill	Animal	Ton on hoof	Hog unit
11	mixed	996	6,053	757
2	cattle	2,189	4,405	875
3	hogs	552	4,697	552
1	mixed*	2,040	6,850	1,080

*Includes paunch manure.

The wastes from a mixed kill in terms of hog units assume that the waste per head of cattle is equivalent to that from 2.5 hogs, while calves and lambs are each equivalent to a hog. Mohlman¹⁰ believes that for losses the most useful unit is "per ton live weight," which is the same as "per ton on hoof."

Character and Strength of Wastes

Stockyards. Stockyards connected with paeking plants are usually provided with catch basins, floored, which may be covered. The strength of the waste varies widely, depending upon the weather, practice of manure removal, and frequency of washing. An analysis of the wastes from a Chicago stockyard²⁵ showed 173 ppm suspended solids and 64 ppm BOD.

Slaughterhouse. In large plants blood is collected and sold or processed for feed and fertilizer. Blood has a BOD of about 165,000 ppm, clots readily, and decomposes rapidly. Paunch manure is usually segregated from the liquid wastes and disposed of separately. The quantity of paunch manure varies from 10 to 40 lbs per animal. Boruff² estimates that a plant killing 10,000 cattle, 20,000 sheep, and 25,000 hogs per week might expect to recover 15 tons of dry weight paunch manure. Carcass dressing, rendering, drainage from the hide cellar, vat waters from hog hair removal, and drippings from the cooling room contribute to the polluting material.

Some average analyses²⁵ representative of combined slaughterhouse wastes, expressed in ppm, are given in Table 7.

TABLE 7

Type Kill	Suspended solids (ppm)	Total Nitrogen (ppm)	BOD (ppm)	Volume per animal gals
General	929	324	2,240	359
Cattle	820	154	996	395
Hogs	717	122	1,048	143

Packing house. Blood is usually collected, coagulated by heating, and filtered. Many smaller plants make no attempt to recover blood. Paunch manure may be dumped or discharged to the sewer. Carcass dressing, hide cellar drainage, eviscerating, tripe washing, sausage making, and laundries produce various quantities of polluting material. Larger plants recover hair and do both edible and inedible rendering. Glue manufacture is usually carried out in separate plants, but a gelatin may be produced for sale to glue works as a raw material. The wastes consist of steep and wash waters. The character of the major wastes¹⁴ of a hog-packing house is indicated in Table 8.

TABLE 8. MAJOR COMPONENTS OF HOG PACKING WASTE¹⁴

	Suspended Solids (ppm)	Organic Nitrogen (ppm)	BOD (ppm)
Killing floor	320	134	825
Blood and tank water	3,690	5,400	32,000
Scalding tub	8,360	1,290	4,600
Meat cutting	610	33	520
Gut washer	15,120	643	13,200
Sausage Dept.	560	136	800
Lard Dept.	180	84	180
By-products	1,380	186	2,200
Laundry	4,120	56	1,300

The weighted average for combined wastes from 38 packing house plants is given in ppm²⁵ as: suspended solids 645; volatile suspended 582; organic nitrogen 113; BOD 909.

The average unit losses in cattle and hog killing operations in 14 Chicago packing houses, expressed as liquid losses in gallons per ton of kill and pollutional losses in pounds per ton, are calculated by Mohlman¹⁷ (Table 9).

TABLE 9

	Liquid	BOD	Suspended Solids	Nitrogen	Grease
Cattle	3,225	28.5	25.3	3.17	2.01
Hogs	4,300	31.4	20.9	3.15	3.29

The hog kills show more BOD and grease per ton. Such losses are reduced by skimming, evaporation, screening, and dry rendering.

Estimates of the total BOD, computed to population equivalent, produced by the slaughter of animals in the United States over a number of years¹⁶ show a material increase. Based upon the average equivalent of 173 persons per ton of mixed kill, the figures are computed in Table 10.

TABLE 10

Year	Animal kill mil. lbs	Tons/day	Population equivalent millions
1930	30,164	50,300	8.70
1935	27,358	45,600	7.89
1940	35,669	59,500	10.29
1945	43,618	72,700	12.58

The maximum loss of 13,670,000 population equivalent occurred in 1944. Comparison of the data published by the United States Department of Agriculture for kill with those for animals killed under government inspection shows that about 35 per cent of the total is local, including uninspected slaughterhouses, retail killing and farm killing.

Pollutional Effects

The pollutional effects of meat plant wastes are similar to those of domestic sewage. The danger of disease from pathogenic organisms in these wastes is slight. The principal deleterious effects are oxygen depletion, discoloration, sludge deposits, seum formation, odors, and insects

Recovery

Reduction of losses by recovering salable products is usually preceded by segregation of wastes from cooling waters. Blood should be recovered as completely as possible. Operators of smaller plants do not realize that one gallon of blood has an equivalent pollutional value of 7 to 8 persons. Larger plants practice recovery and processing of blood. The use of paunch manure as a fertilizer and the production of tankage from rendering processes is common.

One of the most helpful measures in abatement of pollution is recovery of grease by means of screens, vacuators, skimming tanks and grease traps. Mortensen¹⁹ states that a well constructed separation basin should not discharge over 0.2 pound of skimmable grease per ton of kill if operated properly. Grease can be removed by means of baffled tanks or grease traps, 2 to 4 feet deep and not too wide, with detention periods of 30 to 60 minutes, and a velocity of 1 to 2 feet per minute.²⁰ In baffled tanks the under baffle velocity should not exceed 15 feet per minute.

Mechanical devices include continuous removal of grease from the surface and sludge from the bottom. Air is sometimes used to aid grease flotation. Vacuum and pressure tanks are utilized to introduce air bubbles and separate the grease. The air under pressure has a tendency to bring non-fatty substances to the surface and thereby lower the quality of the grease.

Screens are used for retaining paunch manure, cutting and trimming floor wastes, hair and sludges. Stationary, rotating and electrically vibrated fine screens are used. Recovery may vary from 1,500 to 5,000 lbs of wet screenings (80 to 85 per cent moisture) per million gallons of waste.

According to the Institute of Meat Packing²² the percentage of total income from by-products in the meat industry, except hides or pelts, is relatively small, amounting from 3.4 per cent for hogs to 7.2 per cent for calves.

TREATMENT

The degree of treatment required depends upon the dilution available in the receiving stream and legal requirements promulgated by regulatory agencies. The type of treatment process adopted depends mostly upon the size of the industry. Small industries may employ screens, sedimentation basins, sand filters and chlorination, whereas in medium and large size plants coarse and fine screens, sedimentation, vacuation, chemical precipitation, low-rate and high-rate trickling filters, activated sludge and super chlorination have been practiced. Chemical and biological treatment devices require careful control and are suitable for large industries, but small plants require processes which are dependable and simple in operation.

Sedimentation. The early studies by Dilling and Pearse⁴ showed that sedimentation in an Imhoff tank was a satisfactory method for clarification. Removals of 65 per cent suspended solids and 35 per cent BOD, with detention periods of from 1 to 3 hours, produced sludge containing 90 per cent moisture. Howson¹¹ obtained removals of 90 per cent settleable solids and 35 to 40 per cent BOD in the grit and settling basins with a combined retention period of 30 minutes at West Fargo, N. D. Hill¹⁰ reports that plain sedimentation and grease skimming at the Sioux Falls, S. D., packing plant removed 34 per cent BOD and 58 per cent suspended solids after 1.32 hours settling. The raw waste contained an average of 1,650 ppm suspended solids and 1,106 ppm BOD. The same author reports that sedimentation alone for 2.1 hours at Austin, Minn., removed an average of 65 per cent suspended solids and 31 per cent BOD from a waste about one-third as strong as at Sioux Falls. Results obtained by others^{18,21} are of a similar nature. Sedimentation can be considered as a preliminary step in treatment.

Chemical Treatment

A number of precipitants and coagulants have been used in various plants treating packing house waste. Laboratory and plant experimentations have shown that the best coagulation takes place in an acid medium (below pH 6.0). Eldridge,⁶ reporting on laboratory results, found that aluminum sulfate produced a very poor floc, too light to settle, resulting in poor clarification. Ferric chloride and ferric sulfate produced better results, but were not dependable. Chlorine gas produced the best results.

Halverson,⁹ studying the reactions of chlorine gas with the components of packing-house waste, found that 0.2 Cl₂ per liter of waste was sufficient to precipitate the native proteins, but that higher dosages were required to precipitate protein-split products. On the basis of the N/Cl ratios it is more advantageous to chlorinate the native proteins in a very fresh condition or when this ratio is 3:1, since the split products require ratios of 1:40 N/Cl. In the presence of decomposition products a higher Cl/N ratio is required for precipitation. Minimum chlorine requirements to precipitate mixed proteins are obtained at pH 4.2 or slightly less. Chlorination at this pH value liberates CO₂ from protein solutions containing carbonates causing flotation of the coagulum, but mechanical mixing releases the gases and allows the coagulum to settle. This treatment was adopted by the Hormel Packing Co. at Austin, Minn., but was abandoned because of the cost, the toxicity of sludge, and the necessity of excluding much of the waste from the process.

A treatment plant for the Tovrea Packing Co., Phoenix, Ariz.,³ treats waste originating in meat packing, soap, molasses, and liquor distilling plants, including sanitary waste from employees, with the effluent used for irrigation. The average week-day flow of 0.25 mgd is produced between 7:30 A.M. and 6:30 P.M. The waste is mixed with a coagulant, produced from baling wire and chlorine (presumed to be FeCl₃), in a quick-mix flocculation and settled. Using 1,000 lbs of wire and 1,150 lbs of chlorine per million gals, a BOD reduction of 87 per cent (from 1,448 to 188 ppm) and a suspended solids reduction of 94 per cent (from 2,975 to 167 ppm) are obtained. The high BOD reduction is attributed to very complete segregation of blood.

Domogalla⁵ patented a process comprising two-stage chemical precipitation with zinc salts (ZnCl₂ or ZnSO₄) and alum or lime. At the Oscar Mayer plant at Madison, Wis., ZnCl₂ was used with concentrated waste, followed by lime treatment of all wastes, in an attempt to produce an effluent of less than 250 ppm BOD. Reductions of 87 per cent BOD and 93 per cent suspended solids were reported. Lime was used alone later, but it was not as efficient as ZnCl₂.

The use of chlorine and FeCl₃ was reported by Eldridge⁷ to reduce

BOD. Reductions from 2,700 to 310 ppm were obtained. Mortensen²⁰ states that 500 pounds of ferrie sulfate and 1,000 to 2,000 pounds of H_2SO_4 per million gals, at a pH of 4.8, reduced the BOD to 80 ppm. In a plant designed for the Grand Rapids Packing plant, Eldridge⁸ found that the fill-and-draw principle of coagulation and settling, using ehlorine and $FeCl_3$, was well suited to the needs of small packing plants. Small volumes of waste (3,000 to 8,000 gals/day) are held in a tank equipped with a stirring mechanism with a peripheral speed of about 60 ft per minute. Steel or conerete tanks must be protected to prevent corrosion. Application of ehlorine is continued until a light straw-colored liquid is obtained and then 1.5 lbs of $FeCl_3$ per 1,000 gals of waste are added. Stirring is continued for 15 minutes, and the mixture is allowed to settle overnight. Supernatant liquor is returned to the treatment tank and the sludge dried on sand beds or spread on cultivated land.

Biological Treatment

The most extensive studies of biological treatment for meat plant wastes were made in Chicago⁴ during 1912 to 1918. Subsequently, a number of investigators have studied various biological treatment devices.

Trickling Filters. Low- and high-rate filters as well as double filters are used. In all cases, filtration is preceded by screening and settling, and followed by final sedimentation tanks. The low-rate trickling filters in Chicago⁴ removed 81 per cent of the BOD applied. High-rate filters are used at the Hormel plant at Austin, Minn.

Double filtration, based upon studies by Levine¹³ and his associates,¹⁴ was adopted at Mason City, Iowa. Washable primary (roughing) filters, settling, and secondary filters are employed. The primary filters, 4 feet deep, receive a flow of 3 mgd and a BOD load of 1,760 lbs/acre ft, causing a reduction of 29.0 per cent. The secondary filters, dosed at a rate of 1.5 mgd are loaded with 660 lbs BOD per acre ft resulting in a reduction of 62.8 or an over-all reduction of 94.3 per cent. A similar plant at West Fargo, N. D., includes a number of improvements and changes found to be desirable.¹¹ The primary filters, 6 feet deep, are equipped with air and water-wash systems. The operating rate is about 6 mgad, reducing the raw waste BOD from 1,000 ppm to 250 to 350 ppm when loaded at 5,000 to 6,000 pounds per day. The secondary, conventional filters, 6 feet deep, are dosed at a rate of about 1.4 mgad when operated in parallel. The over-all BOD reduction is over 95 per cent.

Several plants providing washable roughing filters, but no final filtrations have been installed.

Activated Sludge. Milling and Poole¹⁵ report results on the activated sludge treatment plant of the Kuhner Packing Co., Muncie, Ind. The plant

has a design capacity of 350 to 500 hog units or a flow of 200,000 to 500,000 gals a day. Preaeration and preliminary clarification are practiced. About 90 per cent of the return sludge is passed to the aeration tanks and 10 per cent to the preaeration tanks. With an aeration time of about 17.5 hrs, about 4.25 cubic feet of air is used per gallon of waste treated or about 780 cubic feet per pound of BOD reduction. The average BOD of 758 ppm was reduced by 44 per cent by the clarifier and an over-all reduction of 98.8 per cent was obtained.

Sand Filtration. The possibility of sand filtration after settling of slaughterhouse waste for smaller plants was indicated in 1891,¹ but considered inadvisable because the acidic conditions in sand filtration prevented nitrification. Experiments²³ showed that dosages of 120,000 gals per acre, representing 1,000 lbs of BOD, produced highly nitrified effluents with a BOD of 2 to 3 ppm. Loadings higher than 1,000 lbs per acre a day caused gradual clogging of the filter.

Digestion. Unpublished laboratory experiments have shown that slaughterhouse waste may be digested in continuous upflow digesters with loadings of 0.1 lb BOD/cu ft digester capacity a day, producing 96 to 98 per cent BOD reduction. Gas production is about 8 cu ft/lb of volatile solids added.

Treatment with Municipal Sewage. Many of the meat plants are located in larger cities and the common method of treatment of the wastes is in municipal treatment plants. Chicago treats meat packing wastes in combination with domestic sewage successfully by the activated sludge process. A number of other cities treat varying amounts of meat plant wastes in municipal plants in ratios varying from 2 to 50 per cent by volume, usually after pretreatment of the wastes before admission to the sewers. Combined treatment results are reported by Hill¹⁰ for the Sioux Falls, S. D., and Austin, Minn., plants, where about equal volumes of packing house waste and domestic sewage are treated under a wide range of climatic conditions. At Sioux Falls, the packing house waste may be treated separately, but at Austin, sewage and waste must be treated together. At both plants the packing house waste is pretreated. Two stages of trickling filters are utilized, but the rates of application and loadings on the primary filters differ greatly. Average results over a 9 month period at Sioux Falls and 5 years at Austin are shown in Table 11.

TABLE 11

City	Rate of Application (mgad)	Primary Filter		Rate of Application (mgad)	Secondary Filter		Over-all Red. (%)
		BOD lbs/acre/ft/day	BOD Removal (%)		BOD lbs/acre/ft/day	BOD Removal (%)	
Sioux Falls	6.12	9,590	40.2	3.16	1070	80.0	72.0
Austin	20.20	15,820	33.0	3.75	1132	72.2	82.8

Wastes from a meat packing plant at Tifton, Ga.,¹² are treated separately first, followed by a combination treatment at the municipal sewage treatment plant. Respective flows are 0.300 and 0.325 mgd. The packing plant wastes are settled, aerated, resettled and placed on a 6-foot deep trickling filter. The city sewage is settled and receives the effluent from the packing plant. The combined wastes are settled and further treated on a low-rate trickling filter. The results obtained (Table 12) show a high degree of purification.

TABLE 12

	Suspended Solids	BOD
Raw city sewage (ppm)	362	260
Effluent meat plant (ppm)	554	1000
Plant effluent (ppm)	30	22
Reduction (%)	93	96

The generally practiced forms of pretreatment used are: sedimentation with or without coagulation, septic tanks, roughing filters, super chlorination, or combinations. More complete treatment includes low and high rate filtration, double filtration, activated sludge, and sand filtration. Discharge into municipal sewers usually requires pretreatment. The percentage BOD removals to be expected by the various treatments are:

Superchlorination	75-85
Settling	25-40
Chemical treatment	70-85
Settling and low-rate filters	80-90
Settling and double filtration	90-97
Settling and sand filtration	95-99
Activated sludge	92-98

References

1. Annual Rpt. Mass. State Dept. of Health 1891, 448.
2. Boruff, C. S., Ill. *State Water Survey Bull.* 32 (1939).
3. Carollo, J. *Munic. Sanit.*, 9, 175 (1938).
4. Dilling, A. W., and Pearce, L., "Report on Industrial Wastes from Stockyards and Packingtown in Chicago" (1921).
5. Domogalla, B. P., U.S. Patent 2, 074,082 (1937).
6. Eldridge, E. F., *Mich. Eng. Exp. Station Bull.* 60 (1934).
7. Eldridge, E. F., *Mich. Eng. Expt. Sta. Bull.* 82 (1938).
8. Eldridge, E. F., *Water Works and Sewerage*, 82, 216 (1935).
9. Halverson, H. O., *Sewage Works J.*, 3, 488 (1931).
10. Hill, K. V., *Sewage Works J.*, 17, 292 (1945).
11. Howson, L. R., *Water Works and Sewerage*, 87, 217 (1910).
12. Hurst, D. H., *Public Works*, 72, 8, 11 (1941).
13. Levine, M., *Am. J. Pub. Health*, 25, 171 (1935).

14. Levine, M., Nelson, F. G., and Dyc, E., *Iowa Eng. Exp. Sta. Bull.* 130 (1937).
15. Milling, M. A., and Poole, B. A., *Sewage Works J.*, 10, 738 (1938).
16. Mohlman, F. W., *Ind. Eng. Chem.*, 39, 637 (1947).
17. Mohlman, F. W., *Proc. Am. Soc. Civil Engrs.*, 74, 1052-1061 (1948).
18. Moor, and Payne, *Ind. Eng. Chem.*, 18, 3 (1926).
19. Mortensen, E. N., National Provisioner April 21 and May 1 (1943)
20. Mortensen, E. N., *Proc. 2nd Ind. Waste Conf., Purdue, Ext. Bull.* 60 (1946).
21. Nichols, M. S., and Mackin, J. C., *Sewage Works J.*, 2, 435 (1930)
22. "Readings on By-Products of the Meat Packing Industry," Univ. of Chicago (1941).
23. Rudolfs, W., and Del Guercio, V., *Water Works and Sewage*, 94, 349 (1947).
24. Texas State Dept. of Health, *Public Works*, 72, 19 (1941).
25. U.S. Public Health Service, *Ind. Waste Guides*, "Ohio River Pollution Control," 78th Congress. House Doc. 266, Supplement D (1944).

6. The Fermentation Industries

C. S. Boruff

*Technical Director, Hiram Walker & Sons, Inc.,
Peoria, Illinois*

INTRODUCTION

During the past two decades the fermentation industries have made material progress in the utilization of their processing wastes. As a consequence the term by-product has become more regularly applied. By-product credits have assumed an increasingly more important role in the economics of fermentation processes. Valuable materials heretofore discarded but now salvaged in the manufacture of ethyl alcohol, butyl alcohol, acetone, beer, wine, and antibiotics include food and feed ingredients, chemicals and biologicals. During World War II, shortages and high prices focused attention upon the necessity of utilizing all of the marketable substances in fermentation residues. This situation, along with development of new methods and refinement of existing procedures, has made these operations practical and generally profitable. The market for the recovered products remains good.

BEVERAGE AND INDUSTRIAL ALCOHOL GRAIN DISTILLERIES

Historical. Both beverage and industrial alcohol may be manufactured in grain distilleries depending on the government permits held. However, except for periods of national emergency, the bulk of industrial alcohol will be produced by the fermentation of molasses and by chemical synthesis. On this basis, and assuming that the consumption of distilled grain beverages will continue at the present per capita rate, the beverage (grain) distillers will process between 40 and 50 million bushels of grain per year. An average recovery of 17 pounds per 56-pound bushel of grain processed would yield 340,000 to 425,000 tons of distillers' feed. In the event of grain shortages, the figure might be substantially reduced.

Stillage Recovery. Before Prohibition, stillage from grain distilleries (referred to then as "slop") presented an acute disposal problem. A few of the larger plants dried the screenable matter. Those who tried evaporation of the screened stillage and drying of the concentrate with

the screenings reported little or no financial advantage. Most of the stillage was wet fed with roughage to livestock, mainly beef cattle. Feeding was at the rate of stillage from $\frac{3}{4}$ to 1 bushel per steer. Some stillage was run into streams. Both methods of disposal caused considerable nuisance. With the advent of Repeal most of the large distillers soon installed screens, evaporators, and driers; many of the smaller distillers merely removed and dried the screenings, and the screened stillage was run to waste. Some small plants disposed of their stillage as wet feed.

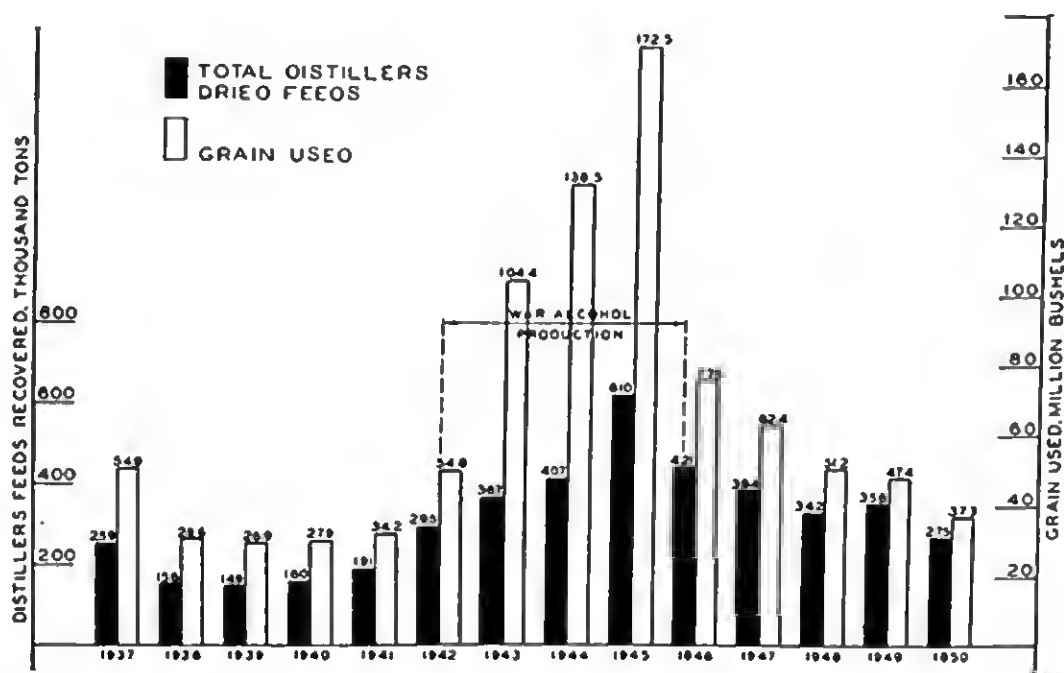


FIGURE 1. Annual production of distillers' dried feeds and bushels (56 lbs) used by grain distilling industry (year ending June 30)

Of the grain used by distillers between 1934 and World War II, recovery as dried feeds ran from 56 to 68 per cent of the commercially potential 17 to 18 pounds per 56-pound bushel of grain processed. Because of the great demand for all feeds during the war, especially protein and vitamin concentrates such as distillers' grains and distillers' solubles, and the government's encouragement and aid in installation of recovery equipment, the end of the war found grain distillers equipped and recovering a much larger tonnage and percentage of potential recovery than during prewar years. An unpublished survey in 1949 by the Distillers' Feed Research Council, Inc. showed that 85 per cent of stillage solids was being recovered as dried feeds by the beverage distillers, 14 per cent was being fed wet, and only 1 per cent was being wasted. This survey checks very well with the United States Department of Agriculture data

covering the entire grain distilling industry. Grain usage and distillers' dried feeds recovery data for the industrial and beverage grain distilling industry are plotted in Figure 1.

Stillage, Amount and Character. Stillage (residue from stills) constitutes the main waste of any volume and strength from a distillery operating on cereal grains. Undiluted stillage contains from 5 to 7 per cent total solids, about half of which is suspended solids. This stillage possesses a 5-day biochemical oxygen demand (BOD) of 15,000 to 25,000 parts per million (ppm) with occasional higher figures having been reported.^{33,77} The volume of stillage will run from 38 to 42 gallons per bushel of grain ground or per 4.2 to 5.2 proof gallons of alcohol produced. Equipment clean-up washings, usually run to waste, are recovered in some plants.

Recovery Process. The first step in recovering distillers by-product feeds from stillage is to pass the stillage through screens (usually 1-mm openings). The removed screenings are then dewatered by pressing and dried in rotary driers. If dried separately, the product is termed Distillers' Dried Grains (light grains). The screened stillage containing about 2 per cent soluble and 1 per cent suspended solids, is sent to multiple-effect evaporators and concentrated to 25 to 35 per cent solids. At this concentration the syrup becomes very viscous, but thin stillage which has been centrifuged or filtered prior to evaporation may be concentrated to as high as 35 to 50 per cent solids.³¹ Chemical treatment, pressure cooking of the stillage, and other treatments prior to the removal of suspended solids will permit even higher concentrations to be obtained through multiple-effect evaporation. None of these latter procedures, however, is considered economically feasible by the industry at the present time.

The centrifuge cake, if produced along with the concentrated solubles from the evaporators, may be readily mixed with the pressed screenings and recycled dried grains to give a uniform and readily dryable material known in the trade as Distillers' Dried Grains With Solubles (dark grains).

The recovery method developed in the Research Department of Hiram Walker & Sons, Inc., which uses centrifuges for removing suspended solids prior to multiple-effect evaporation,³¹ has been working satisfactorily since 1936. This modification throws more of the drying load on multiple-effect evaporators, reduces the drying load on the rotary driers, and in turn the steam consumption per unit of stillage recovered.^{11,16,31} Figure 2 is a simplified flow sheet of the distillery and feed recovery processes.^{1,11}

The syrup produced in the evaporators may be dried separately on drum driers to give Distillers' Dried Solubles. This product was originated by Hiram Walker & Sons, Inc., in 1939 as a pound-for-pound replacement for more expensive dried products used in poultry and other livestock

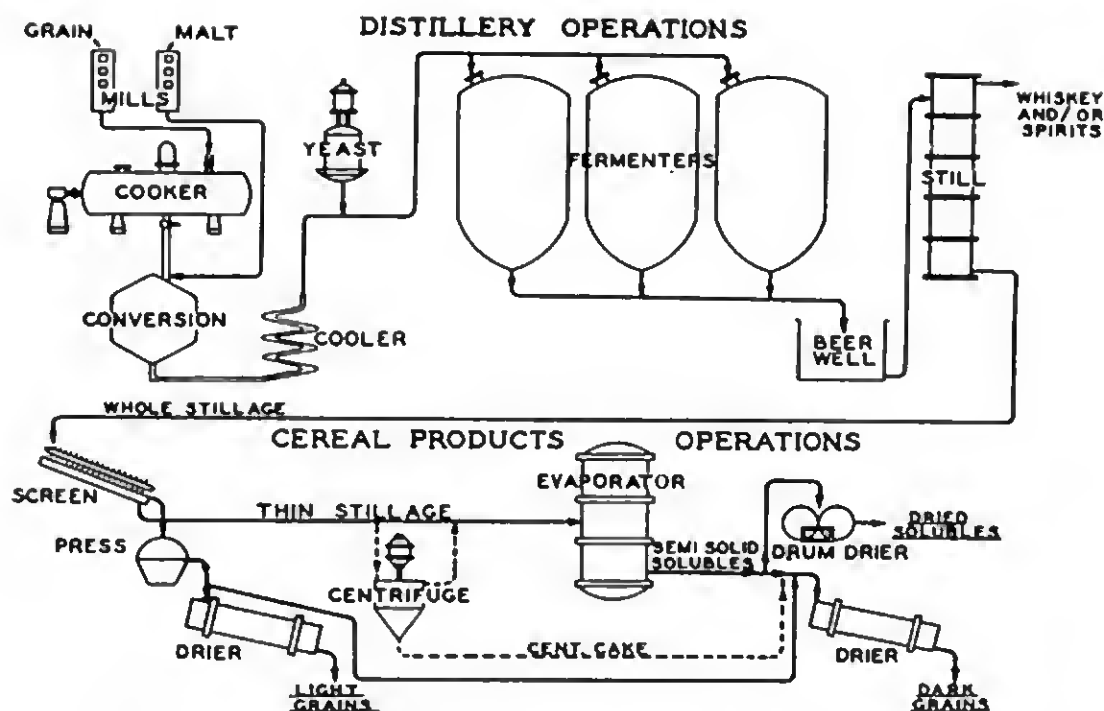


FIGURE 2. Simplified flow diagram showing distillery operations

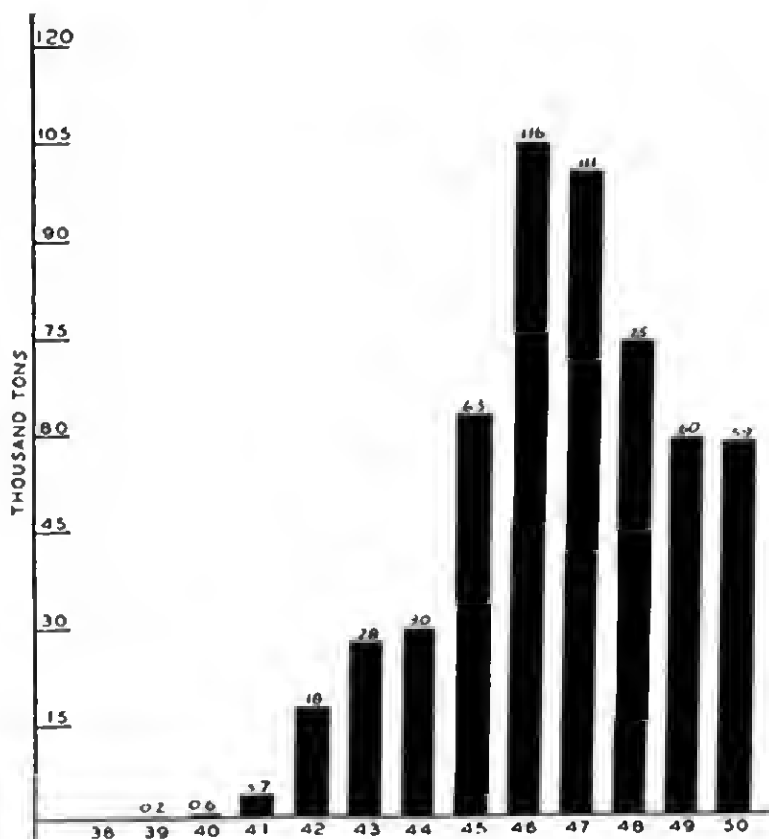


FIGURE 3. Annual production of dried distillers' solubles (year ending June 30)

rations. It came into extensive use during the war period when many other distillers were encouraged to install syrup driers. Figure 3 shows the increase in the production of this material during recent years.

Stillage from an all-rye mash requires the largest outlay of equipment per bushel of grain processed, with an all-corn mash running second. A mixture of grains containing around 70 per cent corn, 20 per cent rye and 10 per cent barley malt requires the least amount of equipment.

Solvent extraction of vegetable oil from distillers' grains was practiced for a time by one distiller¹⁰³ but was discontinued due to the effect on marketing of the de-oiled dried grains and the low market value of the recovered oil.

Analyses and Use of Distillers' Feeds. Table 1 shows typical analyses

TABLE 1. TYPICAL PERCENTAGE ANALYSIS OF DISTILLERS' FEEDS FROM CORN AND RYE PRESSURE-COOKED GRAINS*

	Distillers Dried (Dark) Grains (Grains with Solubles)		Dried Solubles	
	Corn 90%, Barley Malt 10%	Rye 85%, Rye Malt 15%	Corn 90%, Barley Malt 10%	Rye 85%, Rye Malt 15%
Moisture	11	11	5	5
Protein	27	29	25	36
Fat	9	3	6	1
Fiber	7	8	2	2
Ash	6	6	11	11
Nitrogen-free extract**	40	43	51	45

*Analyses vary within small limits because of processing variables and analysis of the cereal grains mashed.

**By difference.

of Distillers' Dried Grains and Distillers' Solubles from mashes predominately of corn and of rye, respectively. Table 2 gives a more complete analysis of dried solubles recovered from processing a mixture of corn and rye.

The protein, fat, vitamin content, lactation factors, and bulk of dried grains make them of special value in dairy rations. The dried solubles with their high soluble protein content and potency of known vitamins and demonstrable but unidentified growth, reproduction, and lactation factors make them a valuable supplement, especially in poultry,^{21,27} swine^{18,80} and calf starter rations.^{90,91} The vitamins found in these feeds come from the grains used as well as from the yeast developed during the fermentation. Boruff and associates have reported on the nutritive value,^{2,4} carotenoids,⁶ amino acids,⁵ and vitamins of distillers' feeds,^{4,34} and the effect of operating variables upon the composition.^{3,34,35} Carriek³⁶ and Hauge³⁷ have discussed respectively, the value of the



(Courtesy Hiram Walker & Sons, Inc.)

FIGURE 4. The role of distillers' solubles in chick rations is laboratory tested

known and unidentified growth factors in Distillers' Dried Solubles. The Distillers' Feed Research Council has summarized⁷⁸ in a series of reports all of the available information relative to the production, chemical and vitamin content, and use of distillers' feeds.

Recovery Costs. The unit cost of a complete stillage recovery plant varies with its size but usually costs as much as the distillery production department. During the war these recovery plants averaged \$23 per annual ton for installations in which rotary driers were used to recover solubles on the screenings. For plants drying solubles as a separate product, the cost averaged \$30 per annual ton. These costs provided for both steam and water demands and a recovery building. Installation costs have subsequently increased materially but the above ratio of costs probably still holds. The estimate of \$26.60 per ton of final product for stillage evaporation and drying costs as given by Kohlins and Demarest⁸⁵ is, in the author's experience, much too low.

The complete recovery of stillage in medium to large size grain distilleries is a profitable operation. In modern plants processing 10,000 or

TABLE 2. AVERAGE CHEMICAL ANALYSIS, AMINO ACID CONTENT, AND VITAMIN CONTENT OF DISTILLERS' DRIED SOLUBLES WHILE PRESSURE COOKING A MASH BILL OF 70% CORN, 20% RYE, AND 10% BARLEY MALT

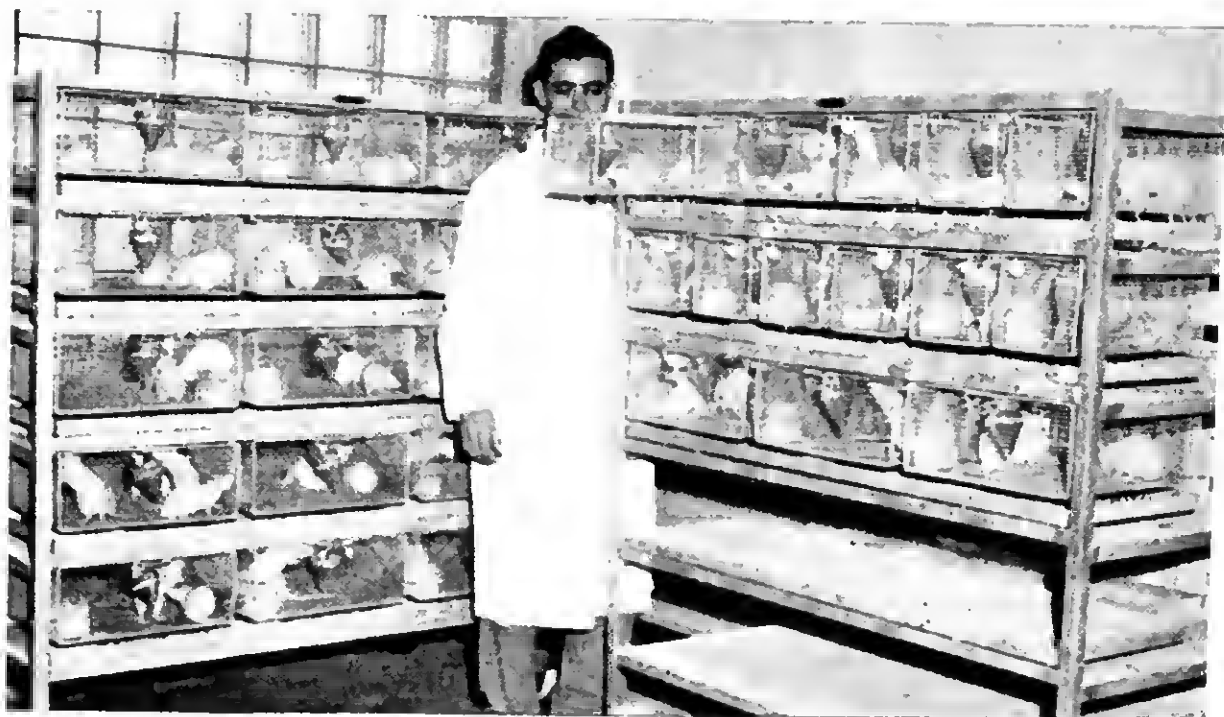
Chemical Analysis	% By Wt	Amino Acid Content (Microbiological Analysis)	% By Wt	Vitamin Content	Meg./G
Moisture	5	Argentine	0.9	Thiamin	7
Protein	26	Glutamic acid*	1.3	Riboflavin	17
Fat	5	Histidine	0.7	Pantothenic	31
Fiber	2	Isoleucine	1.7	Niacin	150
Nitrogen-free ext.	51	Leucine	1.6	Pyridoxin	9
Lactic acid	9	Lysine	0.7	Biotin	0.3
Ash	11	Methionine	0.4	Folic Acid	1.1
Calcium	2.0	Phenylalanine	1.7	p-Aminobenzoic	
Phosphorus	1.9	Serine*	1.4	Acid	10
Sodium	0.4	Threonine	1.0	Choline	6500
Potassium	2.1	Tyrosine*	0.6	Inositol	8000
Magnesium	0.9	Tryptophan	0.1	Unidentified but	
Iron	0.06	Valine	1.6	demonstrable	
Copper	0.01			growth factors	++++
Cobalt	0.00003				
Manganese	0.01				
Silicon	0.1				
Sulfur	0.5				
Chlorine	0.4				

*Reported as not essential in the feeding of man or animals.

more bushels of grain per day, net profit from feed recovery defrays the processing cost of converting the incoming cereal grains to alcohol or whiskey ready to enter the barrel. Even the small distiller can realize a profit on these operations if the installation is properly engineered and operated and steam is produced economically.

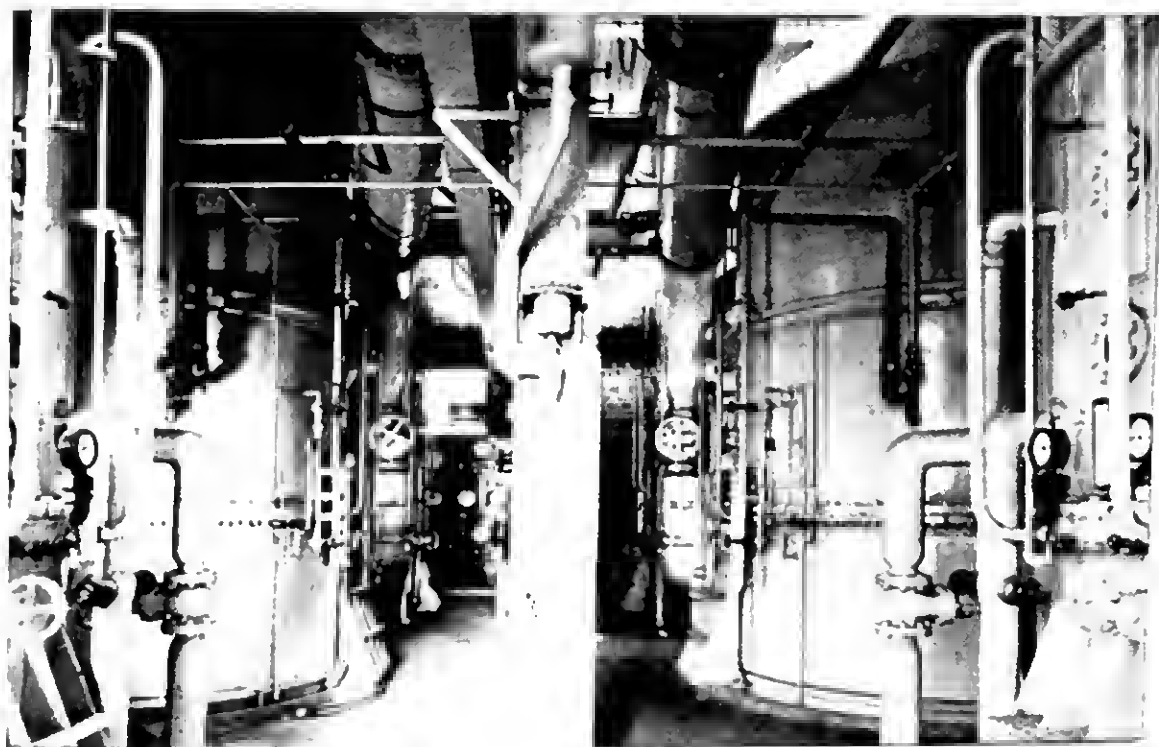
Special Commercial Uses of Grain Stillage and Distillers' Dried Solubles. Screened grain stillage or distillers' dried solubles have been used as good base materials for biochemical productions because of their soluble nutrients and vitamins and other biochemical growth stimulating constituents. For a number of years distillers have used both of these products as a yeast growth stimulant. Since World War II it has become a common constituent in the media used for the production of antibiotics.^{86,87} Recently Boruff and associates⁹² reported on the commercial production from stillage of riboflavin and other B vitamins using *A. gossypii* as the fermenting organism. Boruff⁸³ and Hall¹⁰⁴ have reported a process for the production of vitamin B₁₂ and an antibiotic from stillage. Stillage is being employed for the commercial production of fungal amylase, which may be used as a substitute for conversion malt in the production of alcohol.^{88,93}

Stillage Disposal. The Peoria Sanitary District has thermophilically



(Courtesy Hiram Walker & Sons, Inc.)

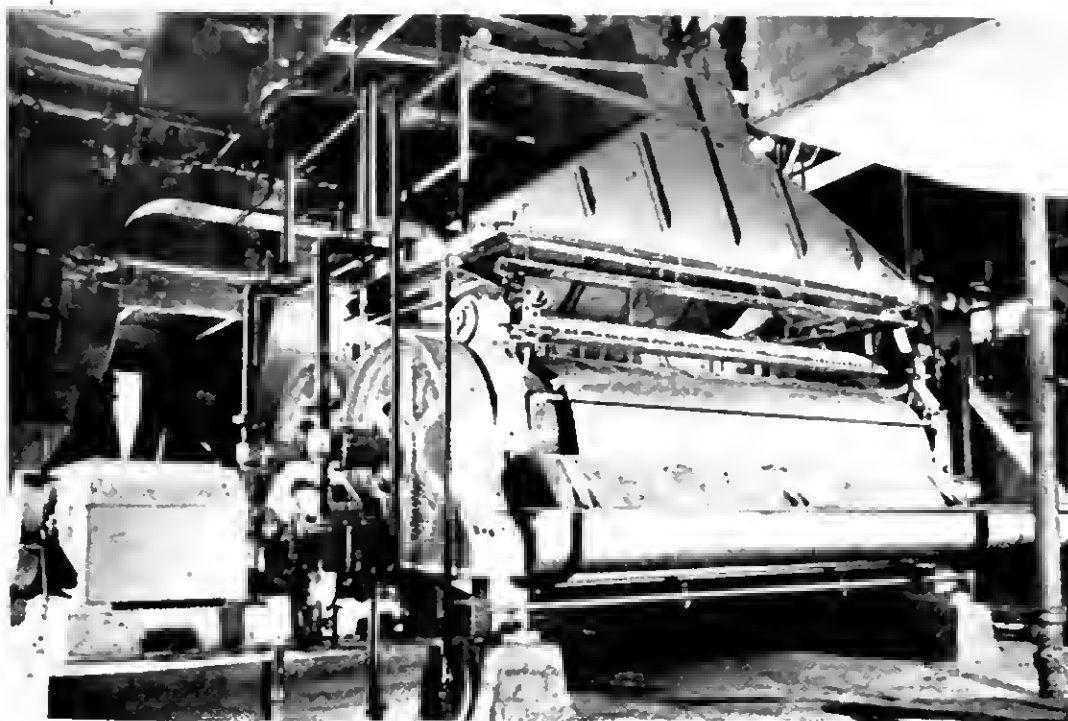
FIGURE 5. Rat colony used in testing nutritive value of distillers' feeds



(Courtesy Hiram Walker & Sons, Inc.)

FIGURE 6. Evaporators used in concentrating distillers' solubles

digested part of the grain and molasses stillage from the Peoria plant of Commercial Solvents Corp. for a number of years.²³ Others have reported studies on the anaerobic digestion¹⁰ and subsequent aerobic treatment of stillage.³³ Broad irrigation and lagooning are used to a very limited extent by some small distilleries. It is reported²⁸ that one acre of land is needed for every 10,000 gallons per day of stillage. In one small dis-



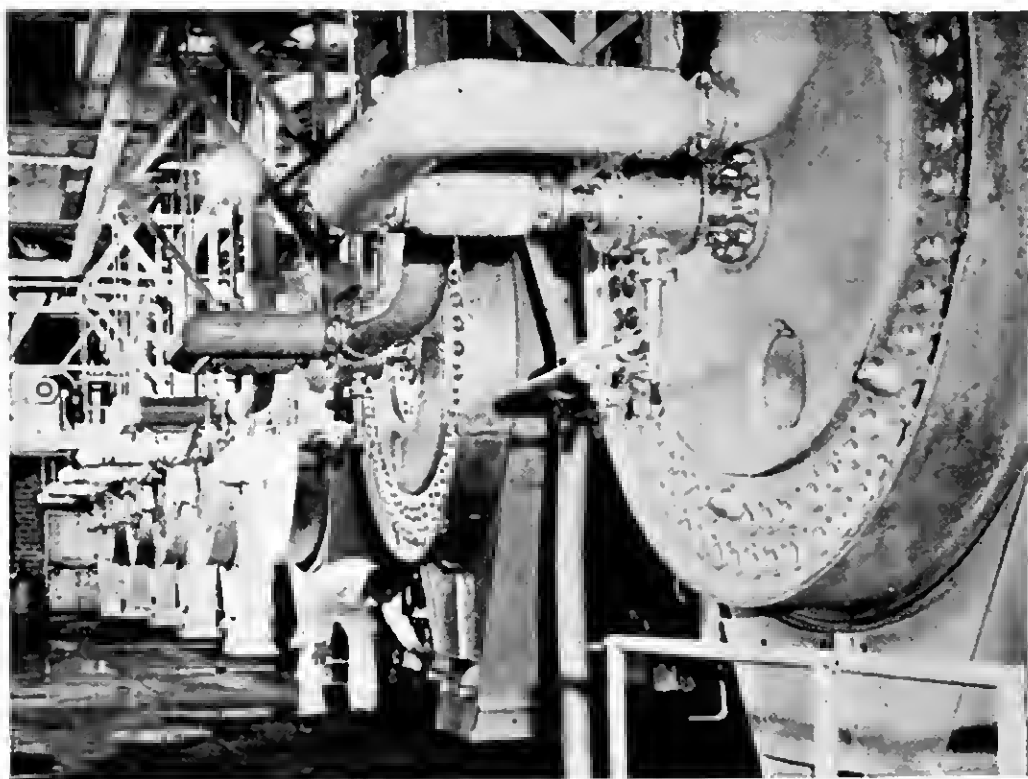
(Courtesy Hiram Walker & Sons, Inc.)

FIGURE 7. Drum dryer used to dry distillers' solubles

tillery, during mid-year when stillage is not taken by farmers, whole stillage is satisfactorily disposed of by lagooning on porous soil at the rate of 5,000 to 10,000 gallons per acre per day. Treatment of the stillage with NaNO_3 at the rate of 10 to 20 pounds per 1,000 gallons aided lagooning stabilization. NaNO_2 has also been found satisfactory in pilot studies. Other processes for the recovery and/or disposal of grain stillage have been studied and proposed.^{9,19,28,29,30}

Pollution Load and Treatment of Wastes from Plants Practicing Complete Distillers' Feed Recovery. Data collected by the Technical Division of Hiram Walker & Sons, Inc., during surveys made at its plants practicing various degrees of stillage recovery, show that the population equivalent of a distillery practicing no stillage recovery amounts to about 50 per bushel of grain processed.¹⁰⁰ Recovery of screenable dried grains will reduce this figure to about 30. As will be noted in Tables 3 and 4, com-

plete recovery of stillage to distillers' dried feeds further reduces the population equivalent load to between 1 and 3. An unpublished sewer effluent survey by Seagrams showed their combined distillery and feed recovery wastes to have a population equivalent load of 2.35 per bushel of grind. Another survey²⁸ reports a figure of 3.5. These data are based on good housekeeping and the recovery of concentrated equipment wash waters into the feeds. Final wastes are carried in large volumes of water. Published data^{77,81} and the data in the right-hand columns of Tables 3 and 4 show that even with complete conversion of grain stillage to dis-



(Courtesy Hiram Walker & Sons, Inc.)

FIGURE 8. Rotary dryers used to dry distillers' grains

tillers' dried feeds, the recovery department still contributes high-volume wastes. Tail water from the evaporators containing some carry-over and volatile acids, along with washings from recovery equipment, constitute more than one-half the pollution load from a medium to large distillery practicing complete stillage recovery.

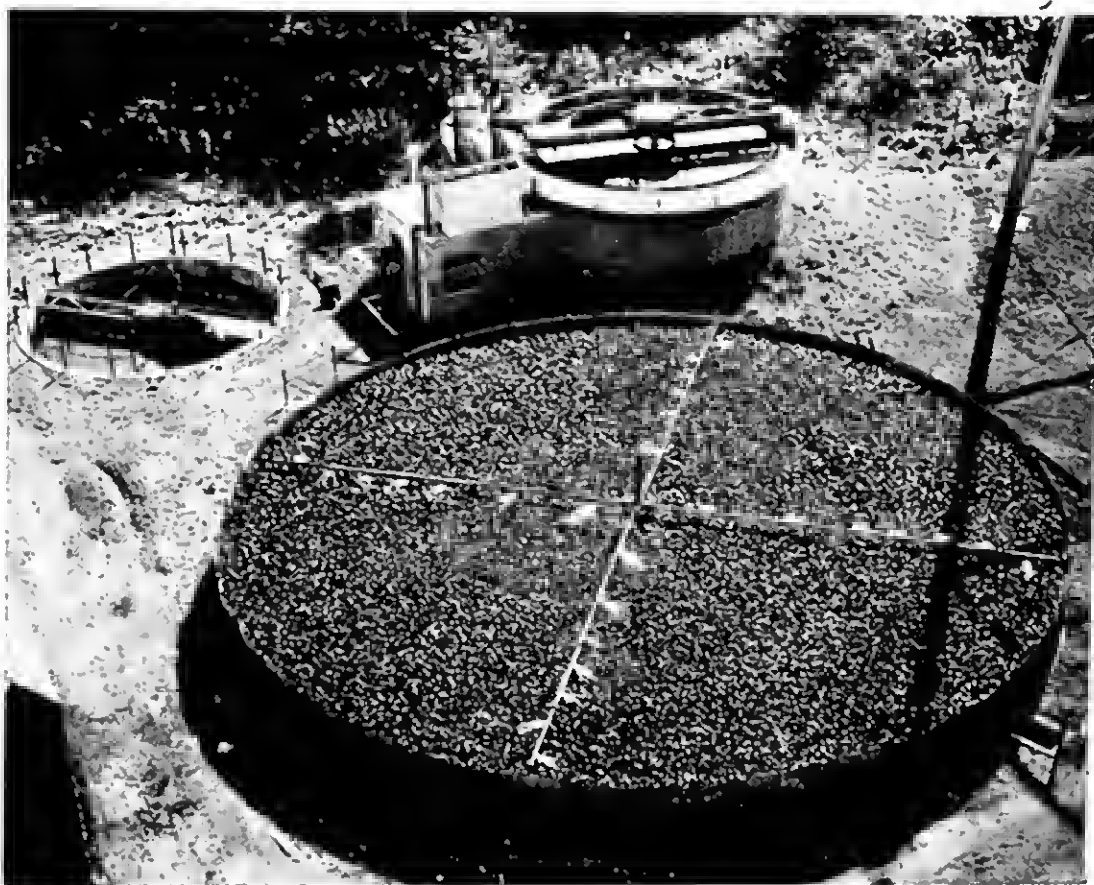
Differences in final pollution load data from different distilleries would be expected due to variations in operating practices, programs, and types of equipment used. Variations such as atmospheric cooking as compared with pressure cooking of grains, ratio of quantity of whiskey to quantity of spirits produced, types of spirit stills used, whether double-pipe coolers

TABLE 3. SOURCES OF POLLUTION LOAD FROM MODERN DISTILLERY PRACTICING COMPLETE STILLAGE RECOVERY*

Source	Volume Gals/1,000 Bu	Total Solids Lbs/1,000 Bu	ppm	BOD Lbs/1,000 Bu	% of Total BOD	Population Equivalent Per 1,000 Bu
Cooking and Fermenting						
Pressure cooker blowdown	3,671	11.5	124	3.8	0.7	22.4
Cooker blow vent stack drippings	24	0.7	500	0.1	0.02	0.6
Cooker vacuum aspirator trap	16,941	7.0	23	3.2	0.6	18.8
Flash cooler (105)	263,428	35.5	17	37.8	7.0	222.3
Flash cooler cleanup	314	9.2	2,025	5.3	1.0	31.2
Fermenter cleanup	3,388	3.2	421	11.9	2.2	70.0
Yeast tub cleanup	847	1.3	128	0.9	0.2	5.3
Total, Cooking and Fermenting	288,613	68.4	26	63.0	11.7	370.6
Distilling						
High wines water	3,097	1.6	256	6.6	1.2	38.8
Fusel oil wash water	47	13.5	89,000	34.7	6.4	204.1
Slop tester drain	48	1.4	1,500	0.6	0.1	3.5
Total, Distilling	3,192	16.5	1,575	41.9	7.7	246.4
Feed Recovery Plant						
Hot well from triple evaporators (tail waters)	254,118	147.5	107	225.8	41.7	1,328.2
Hot well from finishing pan condensers	84,706	17.5	45	31.9	5.9	187.6
Fume chamber scrubber trap for vapors from drum driers	25,412	18.6	275	58.2	10.7	342.4
Dust collector for dried grains driers	10,818	147.2	1,137	102.5	18.9	602.9
Scrubber trap for cyclone on dried grains cooling system	8,706	1.2	29	2.1	0.4	12.3
Scrubber trap for dried solubles airveyor cyclone	536	0.8	45	0.2	0.04	1.2
Equipment cleanup	350	110.0	2,057	6.0	1.1	35.3
Total, Feed Recovery Plant	384,646	442.8	1,331	426.7	78.7	2,509.9
Power house (powdered coal, wet ash and fly ash recovery)						
Total, Power house:	35,000	1,500	43	12.4	1.8	72.9
GRAND TOTAL:	711,451	2,027	92	544	100	3,200

*Data based on Hiram Walker & Sons, Inc., Edmund Street Plant, Peoria, Illinois, operating at 100,000 bu./6-day week, but including 7th day cleanup operations. Domestic wastes to city sanitary sewer. Well water (20% total) used in product processing; river water (32 to 85° F) (80% of total) used for all other purposes.

or vacuum-type coolers are used, types of evaporators and types of dust collectors used, all will materially affect the quantity of solids lost, the volume, and hence the BOD potency and the population equivalent of the waste. The fact that Hiram Walker uses river water sprays in the final stage of their dust collectors adds a pollution load to the liquid wastes by removing some from discharged air. Pattee¹⁰¹ and Davidson⁸¹ have dis-



(Courtesy of Jas. E. Pepper & Co.)

FIGURE 9. Final distillery and feed recovery wastes are stabilized by circulation through two settling tanks and a trickling filter

cussed the effect of evaporator design and operations upon the BOD of stillage evaporator tailings. They report BOD data ranging from 10 to 3,200 ppm, but found most samples to run between 400 and 600 ppm. Others report similar data.⁷⁷

Water usage, and hence plant waste volume (if cooling water is combined with wastes), will vary widely, depending upon equipment, temperature of water used, extent of water recycling, and other normal manufacturing variables.^{81,105} The figure of 711,000 gallons of waste waters per 1,000 bushels of grain processed given in Table 3 is high compared with most distilleries. This is due to the fact that Hiram Walker

uses river water, which during the summer season reaches 85°F, for process cooling, cooling and collecting ash and fly-ash, removal of dust from the final stage of distillers' feeds dust collectors and flash coolers for cooling of its mashes.¹⁰⁵ Well water is conserved and used only for product processing, certain condensers, and as boiler feed. Waste gallonage data from certain of the Schenley plants, where most cooling and barometric condenser waters are reused after cooling in towers, are noted to be quite low (Table 4).

Davidson reported on 24-hour retention time, 5-gallon, continuously fed, anaerobic digestion laboratory studies which showed as much as 96 to 98 per cent BOD reductions in wastes containing 700 ppm of BOD.^{80,81} Davidson also reported that wastes from three of Schenley's plants practicing complete stillage recovery showed a 93 per cent reduction in BOD when the wastes were settled and treated on trickling filters at the rate of 8 million gallons per acre per day (6 ft filter with 4 to 1 recirculation) and 0.75 pounds of BOD per cubic yard.⁸¹ The character of the waste treated on the filters is given in Table 4.

TABLE 4. DISTILLERY AND DRYHOUSE WASTES TO DISPOSAL PLANT⁸¹
(3,000 Bu Per Day Bourbon Distillery With Complete Feed Recovery)

	Gpd**	Total Solids (ppm)	BOD		Population Equivalent*
			(ppm)	(lbs)	
Evaporator condensate	45,000	130	600	225	1,322
Washes	21,000	1,050	1,000	176	1,038
Cooling tower overflow	24,000	1,100	550	110	647
Doubler	3,000	240	1,000	26	153
Domestic sewage	7,000	830	200	14	82
Totals per 3,000 bushels	100,000	610	670	551	3,242
Totals per 1,000 bushels*	33,333				1,080

*Calculated and inserted by Boruff.

**Cooling and barometric condenser waters cooled in towers and reused, therefore gpd data are low.

Glycerol Recovery. While much research has been performed and numerous patents have been granted relating to methods of recovering glycerol from grain and molasses alcohol stillages, there are no industrial installations in operation. Synthetic and soap by-product glycerol will continue to control the market.

MOLASSES DISTILLERIES

Numerous saccharine materials including blackstrap, beet, refiners, and high test molasses are fermented to industrial alcohol and rum. Prior to World War II molasses furnished a substantial part of our industrial

alcohol. The non-fermentable matter which remains as a residue from fermenting molasses varies widely in composition and consequently, in the gravity of the disposal problem. Generally, the fermentation is carried out merely by diluting the molasses with water or stillage to 12 to 18° Bé., adding small amounts of nitrogen and phosphate as yeast nutrients, if needed, and inoculating with yeast. To avoid undue bacterial contamination the pH is adjusted to between 4.0 and 5.0 with sulfuric acid.

Molasses stillages possess a characteristically high pollution load, i.e., a total solids content of 5 to 6 per cent, organic solids content of 4 per cent, and a 5-day BOD in the neighborhood of 18,000 to 22,000 ppm.^{9,38,108} When processing blackstrap molasses the stillage volume runs 10 to 12 gallons per gallon of 190 proof alcohol produced or per 2.4 gallons of molasses fermented. Reich³⁹ reported the chemical composition of some of these residues.

Much of the stillage, except that from the New Orleans and other seashore areas, is concentrated to a syrup in multiple-effect evaporators and used in mixed feeds. From 8 to 12 pounds of such semi-solid syrup are recovered per wine gallon of 190 proof alcohol produced. One semi-solids product (Special Liquid Curbay) which is marketed at a 45 per cent solids content has the following composition:

Distillers' Condensed Molasses Solubles

Crude Protein (%)	5
Mineral Ash (%)	12
Fat (%)	Trace
Fiber (%)	Trace
Nitrogen free extract (%)	27
Riboflavin, μ /g	5-7
Pantothenic acid, μ g/g	5-25
Biotin, μ g/g	1-1.5
Pyridoxin, μ g/g	25
Niacin, μ g/g	40

Some of this semi-solid syrup is also dried and sold as a livestock feed supplement (Vacatone).

Because of its high mineral content (approximately 30 per cent on a dry basis) and hence possible laxative effect, the amount of condensed or dried molasses solubles which can be used in feeds is limited, depending upon the animal. The upper limit appears to be about 3 per cent in poultry rations and 10 per cent in cattle and hog rations. It is especially useful in reducing dusting when mixing rations.

Molasses stillage concentrated to 50 per cent solids and combined with asphalt and inorganic salts has been reported as a satisfactory corebinder in making briquets.⁴⁰

Recovery of potash by incineration of concentrated stillage, although practiced at one time, is no longer economical. In this connection Reich³⁹ has described a process whereby several valuable by-products are recoverable from molasses. Prior to fermentation the molasses is diluted, acidified, and heated, whereupon as much as 88 per cent of the calcium salts is precipitated as calcium sulfate. The precipitate is separated by centrifuging and the clarified molasses fermented. This pretreatment permits the subsequent separation of relatively pure yeast produced during the fermentation. From the de-alcoholized residue after evaporation and destructive distillation, potassium carbonate and refining carbon may be prepared. It is claimed that a distillery processing 50,000 gallons of molasses daily could recover 18 to 24 tons of potash, 10 to 12 tons of activated carbon, 2.5 tons of dried yeast and 3 to 6 tons of calcium sulfate as by-products. The Serralles rum plant in Ponce, Puerto Rico, is recovering feed yeast.

Where feed outlets are not attractive, the dunder may be digested aerobically^{38,41} or anaerobically^{42,43} with a substantial reduction in pollution load. Effluents are rendered sufficiently low in BOD to be disposed of by ponding or in irrigation water. Where anaerobic processes are employed a burnable gas (mixture of CO_2 and CH_4) is produced. A mixture of 1 per cent molasses beer slop and 99 per cent sewage (BOD of 485 ppm) has been given final treatment on two-stage trickling filters, using a recirculation ratio of 3 to 1 and a loading rate of 2,590 lbs of BOD per acre foot, to give a final BOD of 20 ppm, or a 95 per cent reduction.¹¹¹

Lime flocculation in conjunction with bauxite treatment and repeated filtrations has been reported to render dunder innocuous when ponded or applied to sugar cane fields.⁴⁴

Recovery, treatment or disposal of stillage and other molasses distillery plant wastes remain a critical problem for those plants located in the interior or on restricted tide waters.

BUTYL ALCOHOL-ACETONE FERMENTATIONS

The Process. Butyl alcohol, acetone, and small amounts of ethyl alcohol are produced commercially by the fermentation of molasses or grain with *Clostridium acetobutylicum* and related anaerobes. Whey, in small amounts, is also fermented to butyl alcohol and acetone. In processing molasses the sugar concentration is adjusted to 5 to 7 per cent by dilution with water or stillage and the medium is sterilized. Available nitrogen, generally in the form of ammonia, is added in increments after inoculation. Grain mashes of 6 to 8 per cent concentration are thoroughly sterilized and fermented with strains of *Cl. acetobutylicum* which both saccharify and ferment starch. Fermentations are completed in 40 to 65 hours.

Stillages. After the separation of solvents from the beer by distillation there remains a waste containing from 1 to 4 per cent solids. This material is largely organic and ranges in BOD content from 7,000 to 17,000 ppm according to the carbohydrate source.¹⁰ The waste resulting from fermented whey (solvents and other volatile substances) runs as high as 29,000 ppm.⁶⁸

Treatment. These stillages can be disposed of through standard methods of anaerobic digestion followed by aerobic stabilization provided certain operating precautions are observed.^{10,23}

Recovery as Feed. Today most of the butanol-acetone stillage is being evaporated and marketed in dry form for use as a supplement in mixed feeds.^{7,20,68} In the trade the product is known as Dried Fermentation Solubles. One such product, Curbay BG, is made primarily from butyl alcohol fermentation residues. It is a valuable ingredient in high energy rations for poultry and swine. An analysis is given in Table 5. It is a good

TABLE 5. TYPICAL ANALYSIS OF DRIED BUTYL FERMENTATION SOLUBLES (CURBAY BG)

Protein, minimum (%)	10
Nitrogen-free Extract (%)	57
Fiber, maximum (%)	1
Fat, minimum (%)	.05
Minerals, maximum (%)	27
Riboflavin (mcg/g)	80
Biotin (mcg/g)	2.3
Pantothenic acid (mcg/g)	200
Pyridoxine (mcg/g)	25
Nicotinic acid (mcg/g)	90
Choline (mcg/g)	1,450
Folic acid (mcg/g)	5

source of all the B vitamins and is especially rich in riboflavin that is synthesized during the fermentation. Riboflavin accumulation is appreciably greater when the iron content of the medium is restricted, an observation which has led to the development of patented improvements.^{69,70}

From conventional grain fermentations there is recovered, with each pound of solvents, 1.1 to 1.3 pounds of dry residue with a riboflavin potency of at least 45 mcg per gram. Blackstrap molasses yields, per pound of solvents, 2 to 3 pounds of dry substance with a similar riboflavin content. High test molasses, having a lower non-fermentable solids content, gives a by-product of correspondingly higher vitamin potency. Special fermentations result in riboflavin potencies as high as 3,000 and 4,000 mcg per gram for whey⁷⁰ and corn⁶⁹ respectively. In view of the

nutritional value of stillage from butanol-acetone fermentations, complete recovery of residues may now be economically feasible.

BREWING

In 1937 only one of Chicago's 28 breweries recovered brewers' grains in dry form and none recovered surplus brewers' yeast.²⁴ Utilization of these and other brewing wastes as feeds in wet form was the general practice at

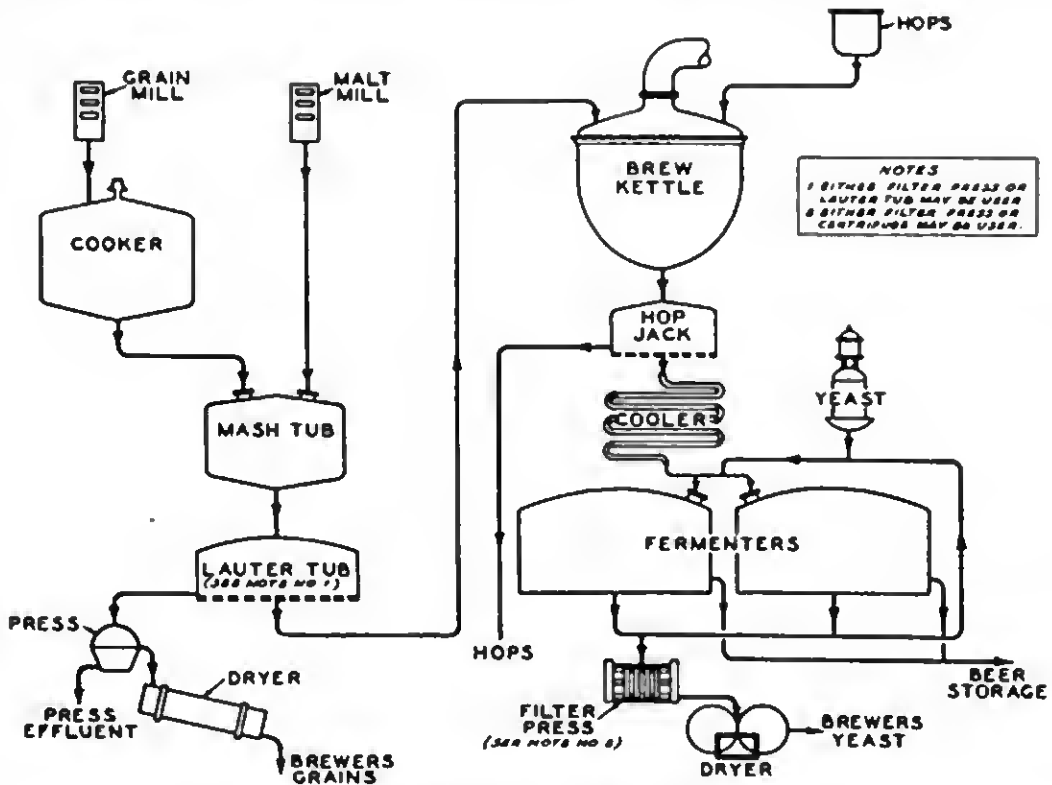


FIGURE 10. Flow diagram showing brewing operations

that time. Subsequently much progress has been made in diverting such materials to foods, pharmaceuticals, and feeds so that currently a large percentage of the industry's more concentrated wastes are salvaged. The form in which residues are finally disposed is influenced by both the size and location of the particular plant. Large breweries find it practical to separate and dry their spent grains and yeast. In smaller breweries, where the volume of residues does not justify the installation of drying equipment, grains and yeast are marketed wet. Liquid wastes too dilute to warrant recovery are either sent to municipal sewage systems or are treated in specially designed systems operated by the brewery.

The Process. Brewing operations are shown in simplified, diagrammatic form in Figure 10. The main by-products, viz, spent grains, hops and yeast are separated as suspended solids at different stages in the process as

indicated. These three materials comprise the recoverable by-products. The waste solids are composed largely of equipment and bottle washings, press and filter liquors and waste beer. Brewers' grains are separated from the wort either in the Lauter tub or by filtration. The separated wet spent grains containing approximately 80 per cent moisture are first dewatered to 65 to 70 per cent moisture by passage through a press and then are dried to about 8 per cent. Of the original grain entering the brewery, an average of 25 per cent (the amount ranges from 23 to 33 per cent, depending upon the proportion of grain to adjunct) is recovered as dry brewers' grains⁴⁹ or is disposed of as wet feed. The average yield of spent grains corresponds to about 10 pounds per barrel of beer produced.

Brewers' Grains. Table 6 gives the analysis and the annual production

TABLE 6. BREWERS' GRAINS

Analysis		Year ¹	Annual Production 1,000 Tons
Moisture (%)	8	1940	117.2
Crude Fat (%)	6-7	1941	168.7
Crude Protein (%)	24-28	1942	232.4
Crude Fiber (%)	15	1943	230.7
Nitrogen-free Extract (%)	39-41	1944	217.4
Ash (%)	4	1945	211.9
Riboflavin (ug/gm)	.57	1946	228.3
		1947	233.1
		1948	232.4
		1949	233.0

¹Year beginning October 1; data from Grain Branch, Prod. and Marketing Adm. USDA.

of brewers' grains during the past several years. Removal of vegetable oil from brewers' grains has been studied¹⁰² but due to lowering of the fat content of the grains and the poor quality of the oil, will probably never be practiced.

Hop Residue. Hops are added to the clarified wort in the brew kettle. After boiling, the insoluble residue, equivalent to 0.3 to 0.5 pounds per barrel of beer, is separated in the hop jack. Dried spent hops have the following composition:⁴⁰

Moisture (%)	8
Crude Protein (%)	18
Crude Fat (%)	5
Crude Fibre (%)	28
Nitrogen-free Extract (%)	36
Ash (%)	6

Although numerous applications for spent hops have been explored, no completely satisfactory outlets have developed. Despite the bitter prin-

ciple which hops contain they have been shown to be palatable to dairy cattle when fed in mixtures with spent grains.^{49,50} In lieu of other disposal methods hops have been used also to a limited extent as a fertilizer and as a soil loosening agent, but they are more commonly burned under the boilers. In the wet state 100 pounds are equivalent to 8 to 15 pounds of coal.⁵¹

Yeast Recovery. During fermentation there is about a four-fold increase in the weight of yeast cells, the total crop approximating 0.6 to 0.8 pounds of dry substance per barrel of beer produced. After providing pitching yeast for subsequent brews, from 0.5 to 0.6 pounds per barrel of beer remains as a surplus. Assuming a yield of 0.5 pounds per barrel of beer, the estimated annual potential of dry brewers' yeast in the United States would be in the neighborhood of 40 million pounds.⁵² However, the installation of equipment for recovering dry yeast in breweries where the annual beer production is less than 500,000 barrels is reported not to be profitable.⁵¹ Consequently, the surplus yeast from smaller breweries is either collected for processing elsewhere or is disposed of with other residues as wet feed. Actually, of the total produced, some 12 to 14 million pounds of brewers' yeast are dried annually, one-third of which is debittered for human consumption.⁵³

The yeast that deposits in fermenters and storage vats is drawn off in a slurry with residual beer, concentrated by centrifuging or filtering, and either drum or spray dried.⁵⁵ The dry product is an excellent source of protein and vitamins and is commonly utilized as a feed supplement. Its composition is given below:

Brewers' Feed Yeast, Dry Basis

Crude Protein (%)	40-45
Crude Fat (%)	0.7-1.5
Nitrogen-free Extract (%)	40
Fiber (%)	5-6
Ash (%)	6-7
Thiamin ($\mu\text{g/g}$)	90-120
Riboflavin ($\mu\text{g/g}$)	60-80
Niacin ($\mu\text{g/g}$)	120-240

Food or pharmaceutical yeast is prepared from surplus yeast by washing and removing the bitter character which is derived from the hops and the metabolites of the yeast. This process involves washing with alkali or propagation under aerobic conditions.^{54,55} Enriched brewers' yeast containing increased potencies of vitamins is produced by permitting the washed yeast to absorb vitamins released from plasmolyzed cells.⁵⁴

Lin¹⁰⁶ has reported on the production and recovery of additional yeast

by fermenting grain press waters. Good growth of *Hansenula* yeast was obtained and the original BOD (22,000) of the press water was reduced by one-half.

Wastes. The total volume of liquid wastes from brewing has been found to range from 180 to 500 gallons per 31-gallon barrel of beer produced.^{15,22,28,49,52} The various items contributing to this total as determined in one survey²² are given in Table 7. The total waste (industrial

TABLE 7. TYPICAL ANALYSIS OF BREWERY WASTES¹

	Gals of Waste/Bbl of Beer	Average 5-Day BOD in ppm	Per Cent of Total Pollution Load BOD
Expellor liquor ²	0.6-1.0	15,000	3.5
Hop press liquor	0.4	7,340	1.1
Mash filter-cloth wash water	2.5	4,930	4.6
Yeast wash water	0.5	7,400	1.3
Beer filtrate from yeast	0.5	69,000	13.3
Equipment wash water, waste beer, cooling water, and sanitary wastes		By difference	76.2
Total, 1 to 5, inclusive	4.5	14,000	23.8
Total waste (sewer samples)	400	660	100.0

¹Distribution of concentrated wastes will depend on equipment used (Lauter tub or filters, etc.)

²Liquid from spent grains press.

and sanitary) on a 5-day BOD basis possessed a population equivalent of 13 per barrel of beer produced. Other surveys reveal figures from 6 to 25.^{22,28,52} Typical analytical results on brewery wastes as reported from various sources are given below:²⁸

Determination	Chicago, Ill.	Louisville, Ky.	Minster, Ohio	Houston, Texas
5-day BOD, 20°C (ppm)	1,200	419	1,028	858
Suspended solids (ppm)	650	244	305	411
Total nitrogen (ppm)	50	—	24	—
pH	6.1	7.4	5.5	—

While press liquor from spent grains (expellor liquor) and other heavy wastes are sometimes combined with the wet feeds, they are not sufficient in volume to justify recovery through evaporation and, therefore, are generally sent to the sewer along with dilute wastes.

Brewing wastes usually are handled satisfactorily after combination with domestic sewage.^{12,24,28} Final wastes from the Pabst plant in Peoria are treated in the city's sewage treatment plant on a fee basis.

Fahr¹⁷ has described a settling, digestion, and trickling filter treatment

which reduces a raw brewing waste having a 5-day BOD of 916 ppm to an effluent of 25 ppm. The sludge after digestion may be dried and used as fertilizer.

Schneider¹⁰⁷ and Havighorst¹¹⁶ have reported waste treatment plant results from the 6,000 bbl/week Lucky Lager Brewing Company's plant in Azusa, California. All recoverable solids are segregated and utilized or removed for safe disposal (brewers' grains, spent hops, surplus yeast, filter cake, beer stabilization solids and caustic bottle washing sludge). Sanitary wastes go to the municipal sewer system. Storm and uncontaminated waters flow into a percolation basin. All other wastes amounting to approximately 2,000,000 gal/week or 9.5 bbl/bbl of beer (equipment washings, drainage from spent grains and hops and rinsing waters) are treated. Sedimentation, digestion, two-stage biofilters with a back-circulation ratio of 2.5 times and sludge drying beds are utilized. Ninety per cent of the final effluent is used for irrigation; 10 per cent seeps from spreading ponds to the underground water table. This plant, built in 1948-49, cost about \$225,000. Typical treatment data are given below. Recent expansion of brewery operations has increased the potency of the wastes as indicated in the last two columns.

Typical Treatment Plant Operating Data

	At Designed Capacity			At Overload Capacity	
	Influent	Effluent	Reduction %	Influent	Effluent
5-day BOD (ppm)	445	65	88	980	84
Total solids (ppm)	770	379	51	1780	654
Suspended solids (ppm)	200	25	88	508	10
Dissolved solids (ppm)	570	354	38	1272	644
Volatile of total solids (%)	67.5	44.7	67.5		
Volatile of susp. solids (%)	73.0	94.0	84.0		
pH	7.4	7.6		9.2	7.9
Dissolved oxygen (ppm)	1.0	3.3			

Bushee⁷⁵ states that when brewery wastes are treated separately, sedimentation, chemical treatment, and biological treatment (trickling filters) remove respectively a maximum of 30, 75, and 92 per cent of the BOD. One separate brewery waste treatment plant, placed in operation in November 1938, utilizes sedimentation, digestion and trickling filters. Operating on a waste volume of 280,000 gallons per day possessing a BOD of 882 ppm and suspended solids of 458 ppm, it has averaged about 92 per cent removal of BOD and 85 per cent removal of suspended solids. Operating costs have been reported as about 2 cents per barrel of beer.²⁸ Another plant using activated sludge treatment has experienced operating difficulties.²⁸

YEAST PRODUCTION

Most commercial yeast is produced by the aerobic fermentation of molasses or steep water fortified with inorganic nutrients. The yeast is separated and washed in a series of centrifugal and filtering operations. Undiluted wastes from yeast plants using molasses as a substrate contain from 1 to 3 per cent solids (51 to 75 per cent organic) and possess a 5-day BOD of 3,000 to 14,000 ppm. From 1.0 to 1.5 gallons of waste are produced per pound of product depending on the materials and concentrations used in developing the yeast. This residue is too low in solids content and food or feed value to justify recovery.

Various disposal methods have been studied. In the process proposed by Buswell and Boruff and first installed (1941) at the Fleischmann Yeast plant in Pekin, Illinois,^{8,25} the waste is freed of its filter aid during a settling period of about 4 hours and is then automatically pumped into the first stage of a series of two or three covered digestion tanks. The novelty and success of this particular process depends upon digestion at 95°F., short digestion times (3.5 days primary, 2.6 days secondary) and controlling the volatile acid and nitrogen content in the digesters through back circulation and other patented procedures.^{13,14,25} When the final digester effluent, at a BOD of 1,000 ppm or less, is diluted with plant condenser water in the ratio of 1 part of digested waste with 15 or 20 parts of condenser water, it gives a nonoffensive effluent that may be run into the Illinois river. Where further treatment of the effluent is necessary (National Yeast Corporation, Crystal Lake, Ill.) this has been accomplished through the use of high-rate trickling filters and final clarification, with recycling of part of the final effluent into the liquor being treated on the filters.^{26,82} The 7.25 ft filter, filled with 2 to 3 inch rock, is dosed with a mixture of one part secondary digester effluent mixed with seven parts of effluent from the final clarifier at a rate of 18 mgad. The 62 ft diameter covered filter is equipped with down-draft ventilation at a rate of 3,000 cu ft/min. The final clarifier effluent (96 per cent reduction in BOD) is diluted with condenser water to a BOD of 44 before it is chlorinated and discharged to a small stream. Practically no sludge is formed during the stabilization because of the high organic and low fiber content of the waste. The process permits heavy digester loadings (0.1 lbs organic matter per cu ft per day); hence large quantities of fuel gas (0.7 to 0.9 cu ft per day per cu ft of tank capacity) are produced.^{25,82}

Rudolfs and Del Guercio⁶⁷ have reported high purification and stabilization of yeast production wastes by the use of sand filters following a period of primary settling. Trubniek,¹¹⁰ using a yeast waste containing SO₂ and BOD values as high as 15,000, has reported tests giving the following BOD removals: by electrodialysis, 40 per cent; by activated

sludge, 40 per cent; by anaerobic digestion for 24 hours, 94 per cent; and by trickling filters, 51 to 85 per cent. Coagulants gave little to no clarification.

The most exhaustive studies on biological treatment of yeast wastes have been published in a series of papers by Rudolfs and Trubnick.¹¹⁶

YEAST FERMENTATION OF SULFITE LIQUOR

In the manufacture of paper pulp by the sulfite process, about 2,000 to 3,000 gallons of strong spent sulfite liquor are produced per ton of product. This liquor contains from 9 to 14 per cent total solids, from 1.5 to 2.5 per cent total reducing sugars, and has a 5-day BOD content ranging from 20,000 to 45,000 ppm.⁴⁵ Considerable variation in characteristics of the liquor is found with the differences in degree and method of cooking the wood chips and in the type of wood used.

The spent liquor is generally discharged with other processing waters into streams and lakes where it poses a serious pollution problem through deoxygenation of the receiving waters. Scope of the waste problem of this industry may better be judged by considering that an average size pulp mill disposes of some 100 tons dissolved wood solids daily, while the U.S. sulfite pulp industry has the problem of getting rid of some 3 million tons annually.

Over a period of 70 years many processes and methods of utilizing or disposing of spent sulfite liquors have been proposed. A few such processes are in active use, but to date the economics and technology of processing such large quantities of organic matter in dilute solution have prevented development of a common answer capable of being utilized by the industry as a whole. Those processes in commercial use are for the most part limited in application by conditions peculiar to particular mills or size of the market for by-products which will bear the cost of treatment. New developments in the field of evaporation and burning of the solids have lately been publicized and are being intensively studied.⁹⁵

Fermentation processes for utilizing the wood sugars have received much attention. Production of ethyl alcohol was initiated in two plants during World War II, one at Thorold, Ontario, and the other at Bellingham, Washington. The former has a capacity of 600,000 to 700,000 Imperial gallons of high proof alcohol per year; the latter about 2.3 million U.S. gallons per year. A third plant at Gatineau, Quebec, having a capacity of about 2.8 million U.S. gallons per year, went into production in 1949. Approximately 22 gallons of alcohol are produced from the liquors from each ton of pulp production.⁴⁶ By combined pretreatment and fermentation, the pollution load of the liquor processed is reduced by at least 40 per cent.^{45,48} A further reduction in the pollution load of this waste can

be accomplished by aerobic propagation of certain fodder yeasts in the alcohol stillage.^{47,96}

Another fermentation process for producing food and feed yeast has been in commercial production at Rhinelander, Wisconsin, since 1948. This plant produces 4.5 tons dry yeast daily and reduces the BOD of the spent liquor processed by about 60 per cent. The greater degree of pollution abatement is derived from the use of *Torulopsis utilis*, a yeast capable of utilizing both hexose and pentose sugars. The process and chemical and vitamin analysis of the yeast produced has been reported on by Wiley, *et al.*⁹⁸

Wiley and others⁹⁹ found they could reduce the BOD of sulfite wastes by about 80 per cent through lime treatment, followed by an acetone-butanol fermentation.

Other biological processes for treating spent sulfite liquor have received extensive study. Standard practices common to sewage plants, such as the trickling filter, activated sludge, contact aeration, and anaerobic methane processes have all been evaluated,⁹⁷ but in general have not yet been found adaptable to the problem.

WINE AND BRANDY

Historical. Wine making in the United States dates back to the earliest colonial settlers and commercial production has been a well established enterprise for more than a century. Prior to Prohibition, wineries were mainly small units located in rural districts near the vineyard grape supply. The renaissance of the industry has been accompanied by progressive expansion and by some centralization of operations. These changes have magnified the residues disposal problem. However, as a result of active research on the composition of winery wastes and on methods for separating valuable by-products, an appreciable percentage of the tartrates and alcohol formerly wasted are now recovered. Furthermore, good prospects have developed for reclaiming other constituents. The major problems remaining upon which research effort is being concentrated are in connection with the satisfactory disposal of pomace and stillage.

Wine Production. In the production of wine, ripe, sound, clean grapes are crushed to give "must" containing juice, skins, seeds, and pulp. Red table wines are made by fermenting the must directly. In white wine production the suspended solids or pomace are removed prior to fermentation. Dessert wines constituting about 85 per cent of the total United States production are prepared by mixing the wine, after partial fermentation, with neutral brandy which arrests fermentative activity. For

additional information on wines, the reader is referred to a recent book by Dr. Cruess.⁷⁶

Residues. Winery and brandy residues from which various by-products are derived consist of pomace, lees, argols or wine stone, and stillage. The latter is the waste material produced by distillation of wine or pomace wash for fortifying spirits. Lees are the sludges remaining in fermenting and aging tanks after the wine is racked (decanted) or refrigerated. Lees contain from 0.1 to 3.0 pounds of potassium bitartrate per gallon depending upon the particular wine and the source of the lees.⁵⁶ Potassium bitartrate, which crystallizes on the fermenter walls and floor, is termed "argols" or "wine stone." It is of relatively high purity, i.e., 70 to 90 per cent, but is comparatively small in volume and provides only minor quantities of commercial tartrates. Wash waters from wineries normally do not carry much of a pollution load. They are run to the sewer or on nearby land.

Tartrates. Whereas tartrates originally were recovered only from the lees and argols, methods developed prior to and during World War II have made possible the commercial separation of tartrates from both pomace and stillage. The steps involved in these methods have been described in detail elsewhere.^{56,57,58} Of the total annual United States requirements for tartaric acid and its salts (approximately 15 million pounds) some 2.2 to 2.4 million pounds of crude and refined material presently are being recovered in the manufacture of United States wines and grape juices.⁵⁶ This amount, a remarkable increase over prewar years, represents about 20 to 25 per cent of the total potential available from the United States industry.⁵⁹

Pomace. Pomace, which consists largely of grape skins, seeds, and pulp, is separated from the must prior to fermentation in the processing of white grapes and after fermentation in the production of red wines. As pressed, it contains about 60 per cent moisture and represents from 10 to 20 per cent of the weight of original grapes. While this material is a source of both tartrates and alcohol the amounts recoverable vary with the particular wine being produced. Pomace resulting from the manufacture of dry red wines contains from 56 to 68 per cent moisture, 7 to 8 per cent alcohol, and about 4 to 6 per cent tartrate, whereas that from white grapes contain about half the tartrate and lesser quantities of alcohol.⁷⁶ In dessert wine making the fermentation is of shorter duration and less tartrate accumulates on the pomace. Moreover, this material is washed and distilled to provide spirits which appreciably lower the tartrate concentration. However, by utilizing a pomace still or the recently-developed Metzner process,^{57,60} either of which is capable of handling solid materials, pomace can be de-alcoholized with or without prior

pressing. The residue from the Metzner process can be conveniently extracted countercurrently with hot water to effect solubilization of the tartrates. With either procedure the final residual pomace after separation from the stillage is considerably reduced in pollution load and may be used as feed or fertilizer.

The following analysis of dried pomace has been given by Cruess:⁶¹

Protein (%)	11 -12.7
Oil (%)	3.3- 7.4
Ash (%)	4.7- 8.1
Fiber (%)	26 -41
"Starch" (%)	7.4- 7.9

It is apparent from the above analysis that pomace is not comparable in nutritional value to brewery or grain distillery feeds and, consequently is correspondingly less profitable to dry for this purpose. A process whereby pomace and stillage, after removal of tartrates, are admixed and dried as feed has been proposed by Pattee.⁶²

Other valuable components of pomace which may be recovered profitably, depending upon the demand, are grapeseed oil and tannin. Pomace is composed of about 25 per cent seeds. The latter vary in oil content ranging from 7 to 19 per cent.^{61,63} To recover the oil the seeds are separated mechanically, dried, and the oil extracted or pressed out. Grapeseed oil has a wide variety of industrial uses and the extracted seed, although low in protein, is a satisfactory feed.

Pomace is a good source of nitrogen, phosphate, and potash and is commonly returned to the soil if no other disposal method is practiced. One ton of pomace of 50 per cent moisture content supplies about 20 pounds of nitrogen, the same amount of potash and 5 pounds of phosphorous.⁶⁴ The recommended application is from 10 to 20 tons of wet material per acre.

Stillage. Stillage, the de-alcoholized effluent from stills producing beverage or fortifying brandy, is the least readily disposable of all winery wastes. With the increase which has taken place in the sale of dessert wine, thereby requiring more fortifying spirits, this problem has become increasingly acute. An average of 16 to 20 gallons of stillage are produced per gallon of neutral brandy (189 proof) distilled. Under the sponsorship of the Wine Institute one laboratory has determined⁷⁹ the composition and characteristics of more than 100 samples of stillage originating in 60 different fruit distilleries. Conventional stillage averaged 1.6 per cent total solids, about one-third of which was suspended solids, largely yeast. It was acidic (pH 3.4 to 4.2) and contained from 0.2 to 0.7 per cent tartaric acid. The oxygen consumed data ranged from 5,600 to 32,000 ppm

(average 12,300 ppm). Five-day BOD data ran about half the oxygen consumed values. Stillages from pomace stills (less than 20 per cent of California production) contained about 3 per cent total solids, largely suspended, and possessed oxygen consumed values of 15,900 to 18,600 ppm. Others have reported brandy stillages possessing BOD values running from 15,000 to 40,000 ppm.¹¹²

The streams and tributaries in the Central Valley of California, where the greater proportion of the distilleries are located, represent an irrigation rather than a drainage system; therefore, disposal of either raw or treated wastes into these streams is not a good or common practice. Generally, the stillage is run into settling basins. Where the basins are overloaded the stillage undergoes anaerobic decomposition producing foul and obnoxious odors. Various types of insects add to the nuisance.

As a part of a research program designed to solve the problem of stillage disposal, an extensive investigation has been carried out by the Coast Laboratories (Fresno, California) under sponsorship of the Wine Institute. These studies, made in collaboration with the Division of Food Technology, University of California, have demonstrated that "intermittent irrigation" can be controlled to give satisfactory disposal.^{32,65} Plots selected for stillage disposal should be level and the soil porous. By rotating dosage to the various plots so that applications are made every seventh day, and with occasional loosening of the soil, it has been found that average stillage can be applied at the rate of 100,000 gallons per acre per week. Pomace stillages require about double this area, whereas waste waters with low solids content require less. With this system seepage is rapid enough that no standing liquid is noted after 48 hours. Disposal plots are scraped clear of dried solids every few weeks. The solids are used as fertilizer in the vineyards. Quick drying in these beds overcome the odor and insect nuisances usually associated with ponding.

By the use of settling tanks, preferably combined with lime flocculation, an appreciable reduction can also be effected in the pollution load of brandy stillage. The cost of lime for such treatment ranges from 15 to 40 cents per 1,000 gallons of waste.⁶⁶ Diluted, lime-treated, brandy stillage has been satisfactorily stabilized on experimental trickling filters at a rate of 125,000 gal of concentrated waste diluted to 250,000 gallons.¹¹²

Where the volume of distilling material is fairly large, i.e., in the neighborhood of 100,000 gallons per day, installation of equipment for the recovery of tartrates from de-alcoholized stillage is usually profitable.⁵⁶ The separation of tartrates may be accomplished either by chemical precipitation^{56,58} or by ion-exchange resins.⁵⁹ The sedimentation prior to

tartrate removal and tartrate precipitation reduces the BOD of the stillage to about 50 per cent of that originally present.⁵⁸

In a few cases in California (Elk Grove, Kingsbury, etc.) wineries have joined with local taxpayers to finance joint waste and sewage treatment facilities. Condenser and cooling waters are reclaimed and reused after cooling by about half of the plants; others use these waters for irrigation purposes.

ANTIBIOTICS

Penicillin. Penicillin production involves the cultivation of molds of the *Penicillium notatum-chrysogenum* group under submerged aerobic conditions principally on corn steep liquor-mineral salts-lactose media.^{113,114} To recover the drug, the mold mycelium is first separated by filtration and the penicillin is adsorbed or extracted from the filtrate. The mycelium, spent filtrate, and wash waters constitute the major portion of penicillin production wastes. The BOD of the wet penicillium mycelium cake as it comes from the rotary vacuum filters has been reported to range from 40,000 to 70,000 ppm.¹¹⁵ Small scale fermentations indicate a total solids content in the wastes of 4 to 5 per cent, about equally distributed between the mycelium and filtrate fractions.⁷¹ BOD values for the filtrate were found⁷² to range from 2,150 to 10,000 (average 4,380) for one plant and from 1,550 to 5,650 (average 3,000) for another. Wash waters were quite variable, ranging from 210 to 13,800 (average 3,420). About 1,000 gallons of waste are produced per kilo of product.

Because of their high pollution load these wastes are not readily amenable to direct treatment in sewage disposal plants. In some areas, therefore, it has been necessary to carry away the mycelium and evaporate and incinerate the spent filtrate. Recent studies of antibiotic wastes by Heukelekian⁷² indicate that anaerobic digestion with slight agitation and pH control or aeration under conditions preventing floc formation are feasible. The former method was found to reduce the BOD approximately 80 per cent and the latter from 70 to 90 per cent. Liquors could then be treated on sand filters to yield final effluents having 35 to 40 ppm BOD which could be discharged to streams.

The combined residues (mycelium and filtrate) from penicillin production have been found comparable in composition to distillers' dried solubles and are especially rich in pantothenic acid.⁷¹ Feeding tests have revealed^{73,109} they are nontoxic to chicks and capable of supplying riboflavin and certain unidentified growth factors. Some producers have installed equipment to recover penicillin residues and one has reported⁷⁴ the satisfactory combination of penicillin and riboflavin dried wastes. Commercially, a total yield of about 0.25 pound of dry residue is obtain-

able per gallon of medium processed. Many penicillium producers dispose of their mycelium cake to feed mixers either as a wet or dried product. A representative analysis of the dried cake is given in Table 8.¹¹⁵

TABLE 8. COMPOSITION OF DRIED PENICILLIUM MYCELIUM CAKE

Ingredient	(%)
Moisture	8
Protein ($6.25 \times \text{T.N.}$)	32
Fat	7
Minerals	20
Crude Fiber	7
Nitrogen-free extract	26
	Meg/g
Choline	3700
Thiamine	6
Riboflavin	37
Pantothenic acid	64
Niacin	7
Biotin	15
Pyridoxine	13
B ₁₂	0.02

Other Antibiotic Wastes. Other antibiotics being produced commercially by fermentation techniques include streptomycin, aureomycin, terramycin, chloromycetin, and bacitracin.^{113,114} Streptomycin spent liquors have a high biological oxygen demand, an average value of 2,540 ppm and a maximum value of 5,900 ppm having been observed.⁷² About 1,000 gallons of such waste are produced per kilo of product.

Hilgart⁸⁴ has reported on the operation of a treatment plant for streptomycin and penicillin wastes. The original waste had an average BOD of 13,000 ppm, an occasional maximum of 30,000 ppm, and a total daily BOD of 3,060 pounds. By aeration, sedimentation, and digestion, followed by trickling filters, final sedimentation and chlorine treatment, the BOD load was reduced to 60 pounds per day.

It is now well known that vitamin B₁₂ is synthesized in appreciable amounts by various species of streptomyces, including those employed for streptomycin, terramycin, and aureomycin production. This discovery in conjunction with the observation that certain antibiotics in the proper quantity are stimulatory to the growth of animals⁹⁴ has resulted in the almost complete recovery of wastes from these fermentations as feed supplements.

OTHER FERMENTATION PROCESSES

No information has been released regarding the wastes from various other fermentation processes such as the production of citric and lactic

acids, calcium gluconate, special riboflavin and B₁₂ fermentations, microbial amylase and the like. It is known, however, that the producers of these products are studying their wastes.

Acknowledgments

The author of this chapter wishes to acknowledge aid and receipt of material from the following:

1. R. J. Allgeier, U.S. Industrial Chemicals, Inc.
2. Alex B. Davidson, Schenley Distillers, Inc.
3. P. J. Kolachov, Jos. E. Seagram & Sons, Inc.
4. S. B. Lee, Commercial Solvents Corporation.
5. J. E. McClary, Anheuser-Busch, Inc.
6. Alex Sigal, Pabst Brewing Company.
7. W. H. Stark, The Vulcan Copper and Supply Co.
8. John C. Sylvester, Abbott Laboratories.
9. A. J. Wiley, Sulfite Pulp Manufacturers Research League, Inc.
10. J. M. Van Lanen, Hiram Walker & Sons, Inc.

References

1. Anon., *Chem. & Met. Eng.*, **52**, 130 (1945).
2. Bauernfeind, J. C., and Boruff, C. S., *Am. Miller*, **72**, No. 1, 182; No. 2, 53; No. 3, 50 (1944).
3. Bauernfeind, J. C., Smith, M. B., Gary, J. C., Baumgarten, W., Gustoff, F. H., and Stone, L., *Cereal Chem.*, **21**, 421 (1944).
4. Bauernfeind, J. C., Garey, J. C., Baumgarten, W., Stone, L., and Boruff, C. S., *Ind. Eng. Chem.*, **36**, 76 (1944).
5. Baumgarten, W., Stone, L., and Boruff, C. S., *Cereal Chem.*, **22**, 311 (1945).
6. Baumgarten, W., Bauernfeind, J. C., and Boruff, C. S., *Ind. Eng. Chem.*, **36**, 344 (1944).
7. Bird, H. R., and Mattingly, J. P., *Poultry Sci.*, **24**, 34 (1945).
8. Black, H., and Klassen, C. W., *Sewage Works Eng. and Munic. Sanit.*, **12**, 74 (1941).
9. Boruff, C. S., *Ind. Eng. Chem.*, **31**, 1335 (1939).
10. Boruff, C. S., and Buswell, A. M., *Ind. Eng. Chem.*, **24**, 33 (1932).
11. Boruff, C. S., and Miller, D. L., *Sewage Works Eng. and Munic. Sanit.*, **9**, 259 (1938).
12. Bushee, R. J., *Sewage Works J.*, **11**, 295 (1939).
13. Buswell, A. M., and Boruff, C. S., U.S. Patent 1,990,523 (February 12, 1935).
14. Buswell, A. M., and Boruff, C. S., U.S. Patent 2,029,702 (February 4, 1936).
15. Coates, E. W., *Modern Brewery Age*, **26**, No. 3, 50 (1941).
16. Cooley, L. S., *Ind. Eng. Chem.*, **30**, 615 (1938).
17. Fahr, L. L., *Am. Brewer*, **79**, No. 4, 19 (1946).
18. Fairbanks, B. W., Krider, J. L., Carroll, W. E., *J. Animal Sci.*, **3**, 29 (1944).
19. Farber, E. Maengwyn-Davies, G., and Wallerstein, J. S., *Chem. Eng. News*, **23**, 617 (1945).
20. Groschke, A. C., and Bird, H. R., *Univ. of Md., Agr. Expt. Sta. Bull.* **A6** (1941).

21. Hill, P. W., Scott, M. L., Norris, L. C., and Heuser, G. P., *Poultry Sci.*, **23**, 253 (1944).
22. Illinois Dept. Public Health, Private Rept. (August, 1941)
23. Kraus, L. S., *Sewage Works J.*, **5**, 627 (1933).
24. Mohlman, F. W., *Modern Brewer*, **21**, No. 1, 35 (1939).
25. Schlenz, H., *Sewage Works J.*, **16**, 504 (1944).
26. Schlenz, H., Buswell, A. M., and Tatlock, M. W., *Sewage Works J.*, **18**, 19 (1947).
27. Synold, R. E., Carrick, C. W., Roberts, R. E., and Hauge, S. M., *Poultry Sci.*, **22**, 323 (1943).
28. Anon., Report of U.S. Public Health Service, Ohio River Pollution Control, 78th Congress, House Document No. 266, Appendix I (Brewery Wastes), 1041, and Appendix VI (Distilling Industry), 1126 (1944).
29. Wallach, A., and Wolman, A., *Sewage Works J.*, **14**, 382 (1942).
30. Wallerstein, J. S., Farber, E., Macngwyn-Davies, G., and Schade, A. I., *Ind. Eng. Chem.*, **36**, 772 (1944).
31. Willkie, H. F., and Boruff, C. S., U.S. Patent 2,165,950 (July 11, 1939).
32. Anonymous, *Wines and Vines*, **28**, No. 2, 22 (1947).
33. Bloodgood, D. E., *Sewage Works J.*, **19**, 607 (1947).
34. Boruff, C. S., and Kolachov, P. J., *Proc., 3d Distillers' Feed Conf.*, 93 (1948), Distillers' Feed Research Council, Inc., 1232 Enquirer Building, Cincinnati, Ohio
35. Boruff, C. S., *Proc., 2d Distillers' Feed Conf.*, 4 (1947), Distillers' Feed Research Council, Inc., 1232 Enquirer Building, Cincinnati, Ohio.
36. Carrick, C. W., *Proc., 3d Distillers' Feed Conf.*, 7 (1948), Distillers' Feed Research Council, Inc., 1232 Enquirer Building, Cincinnati, Ohio.
37. Hauge, S. M., *Proc., 3d Distillers' Feed Conf.*, 3 (1948), Distillers' Feed Research Council, Inc., 1232 Enquirer Building, Cincinnati, Ohio.
38. de Arce, B. D., *Mem. asoc. tecnicos azucar. Cuba*, **20**, 517 (1946).
39. Reich, G. T., *Trans. Am. Inst. Chem. Engrs.*, **41**, 233 (1945).
40. Moore, W. C., and Myers, H. A., *Ind. Eng. Chem.*, **19**, 147 (1927).
41. Gonzales Maiz, J. C., *Mem. conf. anual, asoc. tecnicas ozucar. Cuba*, **19**, 363 (1945).
42. Bergamin, F., *Bol. ind. animal (São Paula)*, **8**, 54 (1946).
43. Symes, E. L., *Mem. conf. anual, asoc. tecnicas azucar. Cuba*, **19**, 383 (1945).
44. Nurse, H. C. et al., *Jamaica Assae. Sugar Technol. Quart.*, **10**, No. 3, 45 (1947).
45. Tyler, R. G., *Sewage Works J.*, **19**, 70 (1947).
46. Ericsson, E. O., *Chem. Eng. Progress*, **43**, 165 (1947).
47. Kurth, E. F., *Ind. Eng. Chem.*, **38**, 204 (1946).
48. Joseph, H. G., *Sewage Works J.*, **19**, 60 (1947).
49. Nissen, B. H., *Proc., 2d Ind. Waste Conf.*; Purdue Univ. *Eng. Bull. Extension Series No. 60*, 82 (1946).
50. Brown, B. M., *J. Inst. Brewing*, **47**, 176 (1941).
51. Weber, P. J. F., *Am. Brewer*, **76**, No. 1, 60 and 157 (1943).
52. Mohlman, F. W., *Sewage Works J.*, **19**, 473 (1947).
53. Feustel, I. C., and Thompson, J. H., *Chemurgie Papers 1946*, Series No. 2, Paper No. 438.
54. Burton, L. V., *Food Industries*, **15**, No. 11, 66 (1943).
55. Weber, P., Siebel, R. V., and Singruen, E., "Brewers' Yeast—A Victory Food," Chicago: A. E. Siebel & Co. (1943).
56. Halperin, Z., *Chem. & Met. Eng.*, **52**, No. 9, 116 (1945)
57. Metzner, E. K., *Chem. Eng. Progress*, **43**, 160 (1947)

58. Marsh, G. L., *Wines and Vines*, 24, No. 11, 14 (1943).
59. Matchett, J. R., Legault, R. R., Nimmo, C. C., and Notter, C. K., *Ind. Eng. Chem.*, 36, 851 (1944).
60. Metzner, E. K., U.S. Patents 2,359,929 (Oct. 10, 1944) and 2,387,165 (Oct. 16, 1945).
61. Cruess, W. V., *Wines and Vines*, 24, No. 11, 31 (1943).
62. Pattee, E. C., U.S. Patent 2,404,398 (March 29, 1943).
63. Valebregue, G., *Wines and Vines*, 24, No. 11, 24 (1943).
64. Jacob, H. E., *Wines and Vines*, 24, No. 11, 20 (1943).
65. Anon., *Wines and Vines*, 28, No. 11, 33 (1947).
66. Anon., *Wines and Vines*, 28, No. 7, 26 (1947).
67. Rudolfs, W., and Del Guercio, V., *Water & Sewage Works*, 94, 349 (1947).
68. De Martini, F. E., Moore, W. A., and Terhoeven, G. E., U.S. Public Health Service, Suppl. Pub. Health Repts. No. 191 (1946).
69. Arzberger, C. F., U.S. Patent 2,326,425 (August 10, 1943).
70. Meade, R. E., Rodgers, N. E., and Pollard, H. L., U.S. Patent 2,369,680 (February 20, 1945).
71. Tanner, F. W., Jr., Pfeiffer, S. E., and Van Lanen, J. M., *Arch. Biochem.*, 8, 29 (1945).
72. Heukelekian, H., *Ind. Eng. Chem.*, 41, 1412 and 1535 (1949).
73. Newell, G. W., Peterson, W. H., and Elvehjem, C. A., *Poultry Sci.*, 26, 287 (1947).
74. Leader, H. G., *Chemurgic Digest*, 6, No. 18, 272 (1947).
75. Bushee, R. J., Wallerstein Labs. *Commun.*, 3, 8 (1940).
76. Cruess, W. V., "The Principles and Practice of Wine Making," 476, New York, The Avi Publishing Co. (1947).
77. Klassen, C. W., and Troemper, A. P., *Sewage Works Eng. and Munic. Sanit.*, 18, 566 (1947).
78. Anon., "Distillers' Feeds," Distillers' Feed Research Council, Inc., 1232 Enquirer Building, Cincinnati, Ohio (1948, 1951).
79. Coast Laboratories Progress Rept., "The Disposal of Winery Wastes," November 30 (1946).
80. Davidson, A. B., and Banks, Jos. F., *Proc., 4th Ind. Waste Conf.; Purdue U. Eng. Bull. Extension Series 68, 94* (1949).
81. Davidson, A. B., *Sewage and Ind. Wastes*, 22, 654 (1950).
82. Tatlock, M. W., *Sewage and Ind. Wastes*, 22, 663 (1950).
83. Boruff, C. S., *Proc., 6th Distillers' Feed Conf.*, 41 (1951). (First printing). Distillers' Feed Research Council, Inc., 1232 Enquirer Building, Cincinnati, Ohio.
84. Hilgart, A. A., *Sewage and Ind. Wastes*, 22, 207 (1950).
85. Kohlins, W. D., and Demarest, E. L., *Chem. Eng. Progress*, 46, 597 (1950).
86. McDaniel, L. E., U.S. Patents 2,538,942 and 2,538,943 (Jan. 23, 1951).
87. Nelson, H. A., Calhoun, K. M., and Colingsworth, D. R., *Advance Absts. 118th Meeting Am. Chem. Soc.*, 16A (1950).
88. LeMense, E. H., Sohns, V. E., Corman, J., Blom, R. H., Van Lanen, J. M., and Langlykke, A. F., *Ind. Eng. Chem.*, 41, 100 (1949).
89. Krider, J. L., and Terrill, S. W., *Proc., 4th Distillers' Feed Conf.*, 21 (1949); Distillers' Feed Research Council, Inc., 1232 Enquirer Building, Cincinnati, Ohio.
90. Knodt, C. B., and Williams, J. B., *Proc., 5th Distillers' Feed Conf.*, 46 (1950); Distillers' Feed Research Council, Inc., 1232 Enquirer Building, Cincinnati, Ohio, and *J. Dairy Sci.*, 33, 809 (1950).

91. Turk, K. L., and Slaek, S. T., *Proc., 6th Distillers' Feed Conf.*, 5 (1951); Distillers' Feed Research Council, Inc., 1232 Enquirer Building, Cincinnati, Ohio.
92. Smiley, K. L., Sobolov, M., Austin, F. L., Rasmussen, R. A., Smith, M. B., Van Lanen, J. M., Stone, L., Boruff, C. S., "Biosynthesis of Riboflavin, *L. Bulgaricus* Factor and Other Growth Factors by *A. gossypii* Cultivated on Grain Stillage—Laboratory and Pilot Plant Studies," *Ind. Eng. Chem.* (In press).
93. Anon., U.S. Dept. Agri., *Tech. Bull. No. 1024* (August, 1950).
94. Whitehall, A. R., Oleson, J. J., and Hutchings, B. L., *Proc. Soc. Exptl. Biol. Med.*, **74**, 11 (1950).
95. Kennedy, E. H., and Caldwell, F. R., *Paper Mill News*, **73**, No. 31, 12 (1950).
96. Locke, E. G., Saeman, J. F., and Dickerman, G. K., Pub. Bd. Rept. No. 7736, U.S. Dept. Commerce (1915).
97. Holderby, J. M., and Wiley, A. J., *Sewage and Ind. Wastes*, **22**, 61 (1950).
98. Wiley, A. J., Dubey, G. A., Lueck, B. F., and Hughes, L. P., *Ind. Eng. Chem.*, **42**, 1830 (1950).
99. Wiley, A. J., Johnson, M. J., McCoy, E., and Peterson, W. H., *Ind. Eng. Chem.*, **33**, 606 (1941).
100. Carson, C. T., *Munie. Utilities*, **88**, 66 (1950).
101. Pattee, E. C., *Proc., Fourth Ind. Waste Conf.; Purdue U., Eng. Bull., Extension Series No. 68*, 122 (1949).
102. Braseh, J. F., Gibbs, P., and Siefker, J. A., *J. Am. Oil Chemists' Soc.*, **27**, 133 (1950).
103. Boruff, C. S., and Miller, D., *Oil and Soap*, **14**, 312 (1937).
104. Hall, H. H., *Proc., 6th Distillers' Feed Conf.*, 37 (1951); Distillers' Feed Research Council, Inc., 1232 Enquirer Building, Cincinnati, Ohio.
105. Rodgers, C. H., *Chem. Eng.*, **65**, 122 (1948).
106. Lin, P. W., *Communs. Master Brewers Assoc.*, 9 (June, 1950).
107. Schneider, R., *Am. Brewer*, **83**, No. 8, 25 (1950).
109. Milligan, J. L., Anderson, J. O., Combs, G. F., and Briggs, G. M., *Poultry Sci.*, **29**, 870 (1950).
110. Trubnick, E. H., *Proc., 4th Ind. Waste Conf., Purdue U., Eng. Bull., Extension Series No. 68*, 109 (1949).
111. Sawyer, C. N., and Anderson, E. J., *Water and Sewage Works*, **96**, 112 (1949).
112. Vaughan, R. H., et al., *Wines and Vines*, **31**, No. 2, 24 (1950).
113. Petty, R. D., *Chem. Indus.*, **66**, 181 (1950).
114. Anon., *Chem. Eng. News*, **29**, 1190 (1951).
115. Sylvester, John C., Priv. Communication (April 25, 1951).
116. Rudolfs, W., and Trubnick, E. H., *Sewage Works J.*, **20**, 1084 (1948), **21**, 100, 294, 491, 700, 1028 (1949).

7. Corn Starch Processes

W. D. Hatfield

Superintendent, Sewage Treatment Plant, Decatur, Illinois

The manufacture of starch, oil, syrup, sugar and cattle feed from corn by the wet-milling process is carried on in 13 huge, modern, fully mechanized plants in the United States. Over 130,000,000 bushels of corn were processed in 1942, the larger plants processing 50 to 100 thousand bushels of corn a day. A bushel of average quality corn of 16 per cent moisture weighs about 56 pounds and yields about 32 pounds of pearl starch, 1.6 pounds of oil and 13 to 14 pounds of feed by the wet-milling process. The feed consists of the hulls, fiber, gluten, corn solubles and often the oil cake meal. In fact, the feed contains nearly everything in the corn kernel except the starch and oil.

Historical

The problem of recovery or prevention of wastes from factories producing starch from corn is an old one. Formerly the only material produced was starch, and all the rest of the corn kernel became waste. Since the rest of the kernel consisted of almost 25 per cent of the dry substance content of the corn and that portion containing all the nitrogenous portions of the corn substance, this was a formidable amount of material even for the smaller factories then in existence.

The recovery of solid feedstuffs came early and reduced the losses to 7 to 8 per cent of the dry content of the corn. Later evaporation and recovery of the steep water solubles reduced the losses to from 2 to 4 per cent of the dry substance of the corn.¹ Commercially the resulting yield of 96 to 98 per cent seemed fairly good, but the stream pollution effect from even a small factory could still assume the magnitude of that from a city of from a quarter million to a half million people. Early in this century the focus of community attention on these problems imposed pressure on the industry to reduce stream pollution. While earliest work was directed toward chemical and physical treatment of the starch plant wastes, Wagner⁵ concluded in 1911 that this attack alone would not

solve the problem, but that further process modifications to prevent the production of such wastes would be the only satisfactory solution.

The waste prevention systems which were eventually worked out and which are in use today fully confirm the validity of this early opinion, although it was not until the early 1920's that real progress was achieved in some plants, such as those at Cedar Rapids, Iowa, Argo, Ill., and later at Decatur, Ill., and other places.

Recovery systems were developed that proved of economic advantage to the plants using them and also gave relief from the stream pollution standpoint. Several patents covering details of these developments were granted, and much litigation resulted following the issuance of these patents. It is not possible to mention and give credit to the many individuals who contributed to these developments, although the names of Widmer, Bartow, Jeffries, Sjostrom and others come to the mind of anyone familiar with the period.

With the settling of patent difficulties in the early 1930's the re-use of certain waste waters in the plants, following what came to be called the "bottled-up" system, was rather generally adopted; losses were reduced to less than 0.5 per cent of the dry substance of the corn. In most cases this so decreased the sewage pollution load as to bring it within the range of ordinary sewage disposal practices.

This chapter reviews recovery practices and subsequent treatment of remaining plant wastes as they exist today. As much as possible it will represent a fair cross-section of industry-wide practices, but since there are individual differences and variation in details of the process from one plant to another, it will represent particular conditions in the plant and sewage disposal works with which the author is directly connected.

The Wet-Milling Process

The wet-milling process consists of steeping the cleaned corn in a dilute sulfurous acid solution which loosens the hull, softens the gluten and dissolves much of the soluble mineral and organic matter of the kernels. The steeped corn is macerated in "degerminating" mills, freeing the germ but not crushing it. The macerated corn is slurried in process-water in which it flows into germ separators where the germ floats and is removed by skimming. Oil is extracted or expressed from the germ. The oil is refined and the remaining oil-cake is sold as such or added to the feed.

The remainder of the kernel is ground between millstones and the starch and gluten slurry separated from the fiber and hull on reels and shakers. The fiber and hulls, known as grits and bran, are added to the feed. The starch and gluten are separated by settling, centrifuging and counter-current washing. Large amounts of water are used in these proc-

esses to affect separations and to dissolve the organic and mineral matter in the milled kernel from the starch and gluten. The gluten flows to the feed house and the starch is filtered and washed on vacuum filters. The water separated from the starch and gluten is called "process-water" and contains from 2 to 4 per cent of the corn in the form of soluble organic and mineral matter. Previous to 1920 this valuable food material was wasted to the sewer. It's recovery is described under the Bottled-Up process.

The gluten, which is separated from the starch, flows to the feed house where it is filtered and added to the concentrate from the steep water evaporators, the bran and grits, the oil-cake and the residues from the oil refinery process. These materials are dried and marketed as gluten feed.

The starch is filtered and washed on vacuum filters. It is dried and marketed as starch, is modified by chemical processes into various forms of modified starch, or is hydrolyzed into corn syrup or corn sugar. The residue from the modified starches is evaporated and returned to the feed driers, or returned to the recirculation process. The syrup is refined and subsequently decolorized in activated charcoal filters. The first portion of the wash from the charcoal filters contains much syrup and is returned to the refining process, but the last portion is too light for recovery and flows to the sewer.

The wet-milling process produces the following main products: corn oil, oil-cake, gluten feed, starch, modified starch, syrup and refined sugar. It also produces "process-water" high in corn solubles from the starch and gluten separation and the starch filters.

The Bottled-Up Process

Before the bottled-up process was perfected in the 1920's the materials wasted to the sewer consisted largely of the process-water from the starch and gluten separations, residues from the modified starch processes, syrup from the back-wash of the bone filters, oil refinery residues, and entrainment and volatiles from the steep water evaporators.

Figure 1 presents a flow sheet of a typical plant in which the manufacturing processes described in this chapter are drawn in light lines and the recirculation and recovery of process water are indicated by the heavy lines, both solid and broken. The figures on the lines show approximately the gallons of water used in the process per bushel of corn ground. The figures on the heavy lines indicate the large amount of process-water from the gluten and starch separation processes which is recirculated to the mill house and steeps. A plant with a capacity of 50,000 bushel a day will recirculate approximately 2.3 mgd. Before the bottled-up process was developed this amount of fresh water was added to the mill house and

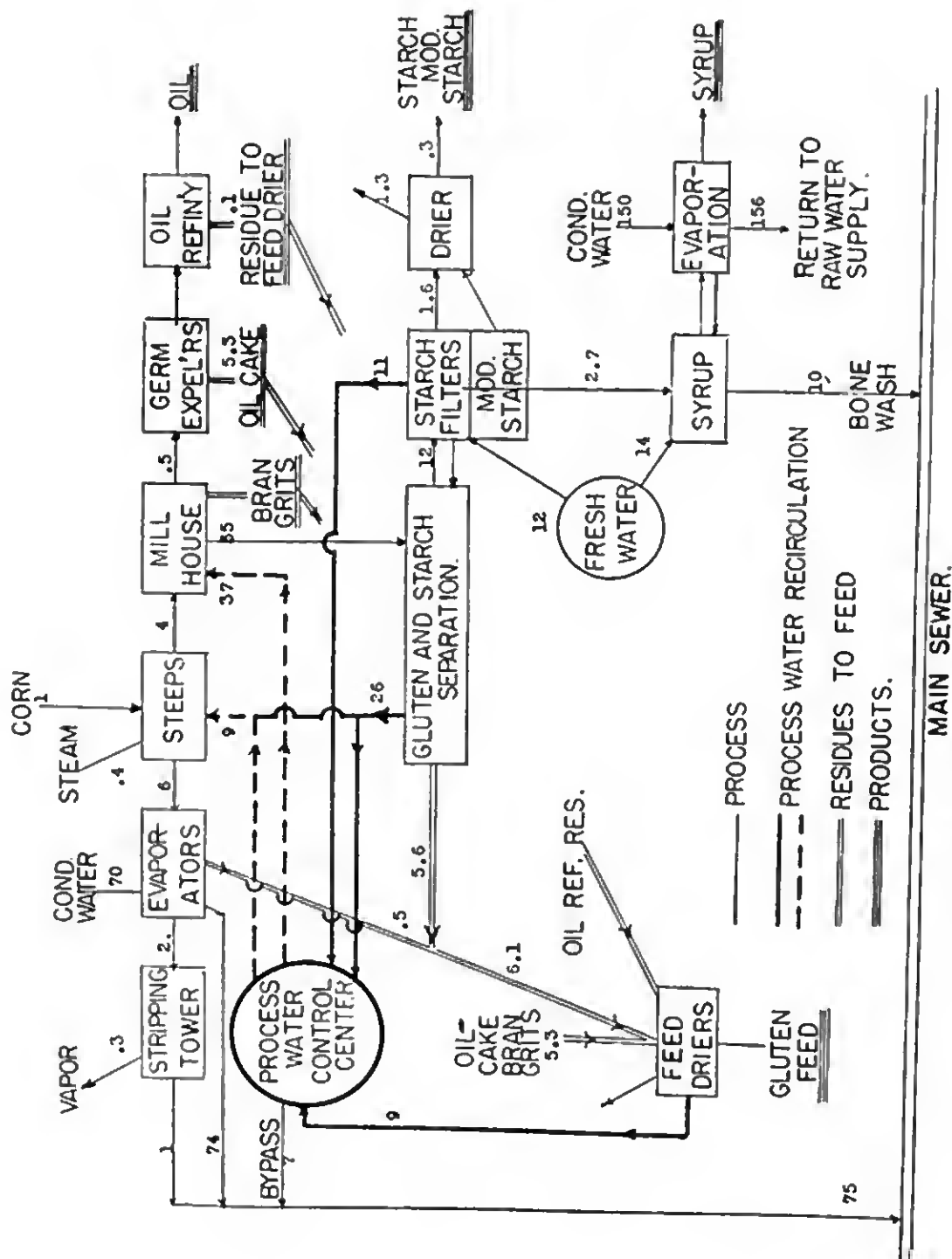


Figure 1. Flow sheet showing corn starch production

steeps. By recirculating this process-water through the mill house, in place of fresh water, the concentration of corn solubles is built up so that it may be withdrawn to the steeps and economically recovered by evaporation. The process water control center shown on the flow sheet is in reality a series of receiving tanks so designed that the heaviest process water is returned to the steeps and the lighter process water to the mill house. In case any excess water goes over the by-pass it is the second wash from the starch filters which contains the lowest amount of corn solubles. When the process is in control there is very little loss of this second wash over the by-pass. There is about 0.7 of a gallon per bushel of water containing large amounts of soluble starch from the modified starch process which is returned directly to the steep water evaporators.

The concentrate from the steep water evaporators, the bran and grits, the oil-cake, the gluten and the oil refinery residues are delivered to the feed drying process approximately as shown by the double lines in Figure 1. Much of the water is removed by filter pressing and is returned to the process water control center. The pressed cake and concentrate are dried in rotary driers.

The bottled-up process may be summarized as:

- (1) recirculation of the process water within the process.
- (2) evaporation of a portion of this recirculated water as steep water.
- (3) adding all organic residues to the gluten and drying to make an improved cattle feed.

This process has reduced the losses per bushel grind from at least ten population equivalent in 1920 to one population equivalent in 1948. In some plants which make a relatively limited amount of modified starch and/or convert a small percentage of the starch to syrup, the losses have been reduced to 0.5 population equivalent per bushel of corn ground.

It is necessary to add some fresh water in the process to wash the starch free of solubles on the vacuum filters, in the modified starch process, and to back wash the bone charcoal filters in the syrup refinery. The vacuum filter wash returns to the milling process and eventually passes out in the steep water, while the heavy syrup washed from the bone filters returns to the refinery. However, as described above, the lighter bone-wash goes to the sewer as waste.

Losses from the Bottled-Up Process. Even though the bottled-up process as described is complete, there are still numerous relatively small losses from plants of this size which get to the sewer. The most important of these are volatile alcohols and entrainment from the steep water evaporators. The volatile alcohols may be recovered by condensation⁴ or removed to the atmosphere in a stripping tower as shown in Figure 1. Entrainment can be kept to a minimum by careful operation of the evap-

orators, but the condenser water including entrainment must go to the sewer. Probably the next most important loss is syrup from the final bone-wash operation and also syrup from the final wash of the railroad syrup cars. These are the wastes which make up the 0.5 to 1.0 population equivalent per bushel. Condensate and entrainment from the syrup evaporators are very low and in most cases may be returned to the raw water supply with the condenser water.

Major losses from the bottled-up process will occur due to a lack of balance between the amount of fresh water added, the amount of recirculation water and the amount of steep water taken to the steep water evaporators. In a complicated process of this type it requires eternal vigilance by a loss control department whose job it is to keep a close control of the operation of all departments at all times. Some losses are due to equipment failures, but many are the result of careless operation of the equipment. Certain types of corn, particularly wet corn received in autumn, cause difficulties in steep water evaporation and in gluten filtration. These difficulties upset the water balance, cause losses of starch wash water by way of the by-pass at the water control center, and increase entrainment from the steep water evaporators. The large amount of this condenser water, which includes this entrainment, is indicated in Figure 1, together with the still larger amount of relatively pure condenser water from the syrup evaporators.

The wastes are: (1) the condensates from the stripping tower, (2) the condenser water and entrainment from the steep water evaporators, (3) the by-pass from the process water control center, (4) the light bone-wash and (5) waters from necessary clean-up operations which cannot be returned to the control center. These losses will vary from day to day, but the average loss from a 50,000 bushel grind when the process is in control, should be about as follows:

Waste	Population Equivalent
(1) and (2) Steep water evaporators	30,000
(3) By-Pass	0
(4) Light bone-wash	8,000
(5) Clean-up, etc.	<u>12,000</u>
Total	50,000

Treatment of the Residual Wastes

The wastes which enter the factory sewers from the process are polluted mostly with organic solubles from the corn kernel, and corn syrup. Therefore, they are amenable to treatment by standard sewage treatment processes, particularly when they are mixed with domestic sewage to furnish the natural bacterial flora for the biological processes.

The sewage treatment processes at Decatur, Ill.,^{1,3} consist of mechanical screens, grit chambers, primary treatment (both Imhoff tanks, plain sedimentation and separate sludge digestion), activated sludge for about one-third of the primary effluent and trickling filters for the remaining two-thirds. The designed capacity of the plant is 150,000 population equivalent. The plant has been in operation since 1928; it treats a mixture of almost equal volumes of the corn products wastes and domestic sewage from a city with an estimated population of 65,000.

The starch wastes are hot and maintain the temperature of the sewage at 80 to 85°F in the winter and 95 to 100°F in the summer. These high temperatures improve the settling characteristics of the solids, the digestion of the sludge in the Imhoff tanks, and increase the loadings possible on the trickling filters. They also increase the decomposition of the sewage in the intercepting sewers and thus the odor hazard of hydrogen sulfide. The hot, slightly septic or near septic, sewage reduces the solubility of oxygen in the activated sludge process, but if loadings are kept below 25 lbs BOD per 1,000 cu ft of aeration capacity, the process produces a satisfactory effluent, although troubles with bulking, on account of the sugar present, are quite persistent.

The mixture of sewage and wastes causes flocculation of some of the waste solids so that the sewage plant receives about twice the normal pounds of sewage solids. The suspended solids concentration in the sewage is between 200 and 300 ppm. The solids settle in the Imhoff tanks yielding an effluent, on one hours settling, of 60 to 70 ppm suspended solids. However, the BOD which is largely soluble is only reduced 25 to 30 per cent. The BOD of the raw sewage mixture is normally about 200 ppm.

The digestion compartment of the Imhoff tanks is maintained at 75 to 85°F by the warm sewage, thus affording good digestion the year around. The digestion compartment loaded at 0.13 to 0.2 lb of settleable solids per cu ft per day, produce a well digested sludge of 6 to 12 per cent solids, containing 35 to 45 per cent volatile solids. The pH value of this sludge varies from 6.6 to 7.0.

The heated separate sludge digestion tank and unheated sludge storage tank are operated as a two-stage digestion process. This process is used to digest the waste activated sludge with occasional seeding from raw storm water sludge or digested Imhoff sludge. The loading of waste activated sludge on this process is about 0.07 lb/cu ft on the heated primary digester or 0.035 lb/cu ft per month on the two-stage process. The digested activated sludge is lagooned without odor nuisance. The supernatant liquor from both primary and secondary tanks is returned to the activated sludge reaeration tanks.

Two-thirds of the settled sewage, having a BOD of about 150 ppm is

applied to standard rate nozzle-type trickling filters, 6 feet deep, at average loading rates of 400 to 900 lbs BOD per acre ft per 24 hours. The effluent produced contains 15 to 30 ppm BOD and 2 to 5 ppm nitrates. Apparently because of the high temperatures the filters slough continuously. The suspended solids in the settled effluent vary between 30 and 45 ppm because the secondary settling capacity is somewhat limited.

The activated sludge process treats about one-third of the settled sewage. If the process is operated in the normal way, it is subject to continuous bulking trouble because of shots of industrial waste and to the sugar present in the wastes. If the loading is maintained below 25 lbs BOD per 1,000 cu ft of aeration capacity per 24 hours, the activated sludge may be kept under control. However, this is difficult unless the corn products wastes are also under very good control. Heavy shots of glucose, starch or process water very quickly overload the aeration capacity causing a rapid growth of the sludge and expansion of the sludge volume as well as an increase in filamentous types of organisms. These latter organisms do not necessarily cause "bulking" of the sludge, but their presence in a light-fluffy sludge greatly aggravates the bulking condition. Sludge indexes of 150 to 350 have been quite common, and if the final settling tanks are not overloaded a good effluent containing not more than 20 to 30 ppm of suspended solids is obtained. However, such operation is easily upset and wasting of thin activated sludge becomes a problem.

There are 6 aeration tanks at the Decatur Plant. For a number of years, 2 of the tanks, or one-third of the total aeration capacity, has been used for reaeration of the return activated sludge, allowing about 15 hours of reaeration of the return sludge and reducing the average sewage aeration period from 5.7 hours to 3.8 hours. This reaeration smooths out the troubles in plant operation by keeping the sludge in a well oxidized condition, particularly that sludge which has received shock loads for a few hours.

Since the process is in need of nitrogen to assist in the biological oxidation of the sugars and starches, return of the supernatant liquor from the sludge digestion tanks to the sludge reaeration tank has been practiced for several years. This not only furnishes nutrient material for the organisms but also solves the vexing disposal problem of digester supernatant liquor. The regular daily return of 200 to 300 ppm ammonia nitrogen in the supernatant liquor to the reaeration tanks allows some nitrification in the reaeration tanks and maintains a lower sludge index, thus reducing the "bulking" problem.

The next step in weighting down the light activated sludge is the occasional addition of well digested sludge from the primary digestion tanks (Imhoff tanks). It is easy to start up an activated sludge plant by aerating Imhoff sludge diluted with sewage for 24 hours. The black sludge turns

rapidly brown and within 2 to 3 days the plant is operating at capacity. This newly developed activated sludge has a sludge index of 20, but in a few days rises to 50 or 60 and has often remained there for 30 to 60 days without further change. However, occasional additions, once or twice a month, of digested sludge may be necessary to keep the sludge index in this desirable region.

Controlling the sludge index by the return of digestion tank supernatant liquor and occasional shots of digested sludge has made it possible to handle with ease loads of 40 to 45 lbs of BOD per 1,000 cu ft per 24 hours producing effluents of 10 to 15 ppm BOD. Further, loads of 65 to 75 lbs per 1,000 cu ft per 24 hours have occasionally been handled.

The residual wastes from the bottled-up process of the corn milling wastes can be treated by the standard biological processes used in sewage treatment. The problem may be somewhat more difficult where the wastes are not mixed with a city sewage, but the rates of treatment indicated by 20 years experience are higher than those usually accepted for domestic sewage alone.

Acknowledgment

The author wishes to acknowledge the excellent assistance given by his colleagues Drs. R. E. Greenfield and G. N. Cornell with whom a previous article² on this subject was published, and who have been most generous in their suggestions for this chapter.

References

1. Greeley, S. A., and Hatfield, W. D., *Trans. Am. Soc. Civil Engrs.*, **94**, 544-99 (1930).
2. Greenfield, R. E., Cornell, G. N., and Hatfield, W. D., *Ind. Eng. Chem.*, **39**, 583-88 (1947).
3. Hatfield, W. D., *Sewage Works J.*, **3**, 621-35 (1931).
4. Pulfrey, A. L., Kerr, R. W., and Reintjes, H. R., *Ind. Eng. Chem.*, **32**, 1483 (1940).
5. Wagner, T. B., *Ind. Eng. Chem.*, **3**, 100-3 (1911).

8. Wastes from the Tanning, Fat Processing, and Laundry Soap Industries

Edward W. Moore

*Graduate School of Engineering, Harvard University
Cambridge, Mass.*

There are a number of industries which produce wastes characterized by a high content of organic matter, but which also contain a considerable portion of inorganic materials introduced in process. The wastes from these industries rank among the heaviest and most polluting of all industrial wastes. Tannery waste is the outstanding representative of this group, but wastes from the processing of animal and vegetable fats and oils and the manufacture of soap also come within the scope of this definition.

TANNERY WASTE

Tanning is an industry deriving from prehistoric times, and to those familiar with them, the wastes from the industry present many Neolithic characteristics, notably a disagreeable appearance, a bad smell, and a high degree of intractability. Despite the best efforts of its chemists, the industry still remains in many respects an art, resistant to exact technical control. The march of technology has, however, enlarged the size of tanning establishments and reduced their numbers. Sutherland¹⁸ notes that there were 7,569 tanning establishments in the United States in 1869, whereas in 1944 the number had shrunk to 477. The waste problem has been concentrated along with the concentration of operations. Massachusetts and Pennsylvania were the first states to recognize tannery wastes as an important factor in sewage treatment and in stream pollution, but the industry is not a localized one, and many other states and municipalities have had to give consideration to the problem.

Although almost any animal skin can be converted into leather, the tanning of cattle hides, sheepskins, and goatskins accounts for the bulk of production, and the manufacture of specialty leathers is not of great interest to those concerned with waste control. In terms of tonnage and value the tanning of cattle hides ranks first and consequently has received

most attention in the literature of industrial wastes. As a matter of fact, the processes and the wastes resulting are little more variable among the different types of skins tanned than they are among different tanneries producing the same kinds of leather. The differentiation of plants into those producing vegetable-tanned leathers, and those producing chrome-tanned leathers is of more importance with respect to waste control than is consideration of the type of skin tanned.

TANNING PROCESSES

All animal skins consist of three layers, the epidermis (cuticle or outer layer), a layer of fatty tissue, and the inner layer, or corium. It is the latter from which leather is made, and the objective of the tanning process is to strip off the two outer layers and to subject the corium to the action of agents which convert it from a semi-soluble protein to the tough insoluble mass known as leather. The principal constituent of the corium is the protein collagen, $C_{102}H_{149}N_{31}O_{38}$, which, in contact with warm water, is converted to the lyophilic colloids gelatin and glue. When subjected to the action of tanning agents, it undergoes a transformation the exact nature of which is unknown, and becomes insoluble in water, tough, flexible and highly durable.

No clue to the nature of the change is obtained from an examination of the tanning agents used, for these are three radically different kinds of substances. The vegetable tannins are complex glucosides of tannic acid, obtained from various tree barks, woods, and fruits. In point of tonnage used the most important are chestnut and hemlock barks, quebracho wood (Argentina and Paraguay), mangrove bark or cutch (Philippines), and myrobalan (India). The tanning agents are usually prepared by water extraction of the crude material and concentration of the extract. Salts of the metal chromium form the second important group of tanning materials. These may be either the trivalent or the hexavalent form. Aluminum sulfate is used for some specialty products. Oils form the third group, but these are used only for special types of leather, particularly chamois. The following data, taken from a publication of the Tanners' Council of America, show the kinds of leather produced by each of the processes mentioned.

Process	Leathers Produced
Vegetable	Sole, harness, and belting Luggage and upholstery Some upper leather
Chrome	Upper leather Glove and garment leather
Combined vegetable and chrome	Some sole and upper leather
Alum or alum-chrome	White upper leather, furs
Oil	Chamois

Vegetable Tanning

A simplified flow sheet of the vegetable tanning process is shown in Figure 1. Each step illustrated in the flow sheet represents a group of operations directed to a single purpose, but it must be borne in mind that much variation exists in individual tanneries.

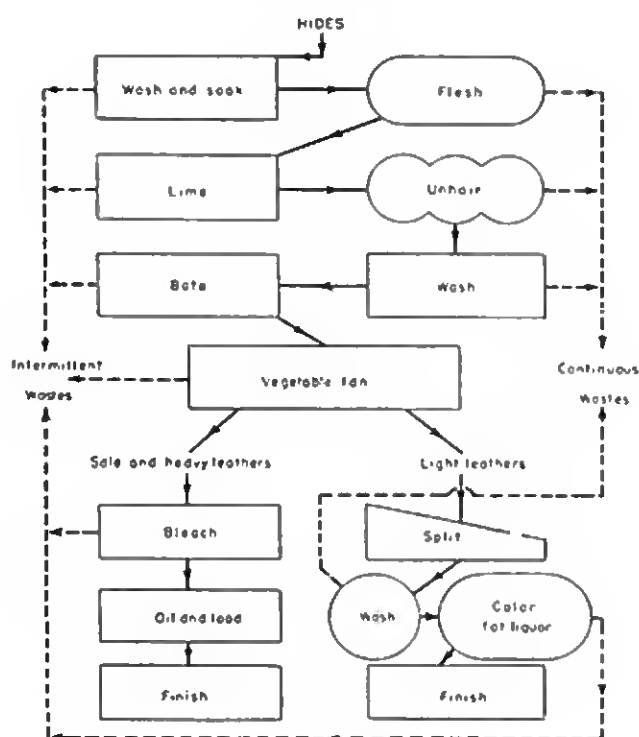


FIGURE 1. Flow sheet of the vegetable tanning process

Hides may be received by the tannery in any one of several conditions: fresh, green-salted, sun-dried, or dry-salted. Fresh hides are not common, the bulk of the hides produced at slaughterhouses being salted and stacked in hide-cellars to await shipment to the tannery. These are the green-salted hides. Hides received from foreign countries are likely to be dried, or salted and dried; these are stiff and hard, and require special treatment.

All hides are first washed to remove blood, dirt, and free salt. This may be done in vats as an integral part of the soaking process, or if a rapid wash is required, it may be done in a "wash wheel," a large drum mounted on trunnions, which receives the hides and wash water and tumbles them by rotation on its axis. These drums are a characteristic feature of the tannery and are used in many of its operations. The waste produced in the washing operation is not differentiated from that produced in the soak.

For the purpose of removing salt, and to soften the hides, they are next suspended in vats of cold water, with frequent changing of the water in the vat or countercurrent movement of the hide from vat to vat. The dura-

tion of this soaking operation depends on the condition of the hides. For green-salted hides it is about 12 to 24 hours; dry-salted hides require several days, while fresh hides may require only the washing. The wastes from the combined washing and soaking operations, known technically as "soaks," contain dirt, dung, blood, some hair, and salt. They are a dark olive-green in color and highly putrescible. The discharge is intermittent.

Fleshing is the next step in the process. This is the removal of muscle and fatty tissues adhering to the underside of the hide. In the modern tannery fleshing is done by a machine which brings revolving knives against the hide while a stream of water carries away the particles removed. In some tanneries the fleshing operation is deferred until after the liming and unhairing. Since the waste contains fatty and fleshy particles in suspension, it is one of the more putrescible fractions. In the ordinary tannery it is discharged more or less continuously.

In order to swell the skins so that the tanning agents may penetrate, and to loosen the hair and the epidermal layer so that they may be removed, the hides are immersed for 5 to 10 days in a suspension of lime hydrate. The liming solutions also contain accelerators which hasten the swelling action; these may be sodium sulfides, amines, or other alkaline reducing agents. The liming process also serves to remove grease from the hides. The operation is performed in vats, on a batch or semi-batch basis, so that the discharge of the lime wastes is intermittent. Sometimes the last vat to receive the hides contains a lime suspension maintained at 90°F. Although relatively small in volume, the lime waste is one of the heaviest of the waste fractions and accounts for some of the more conspicuous characteristics of tannery waste.

Unhairing is accomplished by machines in which knife-bearing rollers sweep over the skin and remove the loosened hair and epidermis, which are flushed off in a stream of water. The hair is separated and washed in clean water. The waste from this process contains fine hair which escapes the screens, together with particles of epidermis and of lime. Discharge is continuous.

The unhaired hides are then given a vigorous washing in clean water to remove lime. This operation may be conducted in drums or in vats supplied with a steady flow of clean water. The waste from the washing operation is relatively large in volume, but of low strength.

The next operation, known in the trade as "bating," has two functions: the removal of the lime absorbed by the skins, and the hydrolysis of some of the proteins which are undesirable in the final leather. Originally, the bating baths were water suspensions of bird or dog dung, which must have made a considerable contribution to the pollutional effects of the waste. Later, "drenches" of fermenting bran suspensions were substituted. In

modern tanning the bate is a solution of a proteolytic enzyme, such as pancreatin or trypsin, plus an acid salt, such as ammonium sulfate. The former removes the unwanted proteins such as elastin and keratose; the latter takes out the absorbed lime. As a waste producer, the process is of little importance, since the bating baths are discharged infrequently and carry no great amount of polluting material.

The hides are now ready for the tanning operation, in which they are placed in intimate contact with solutions of tannin extracts for an extended period. This is usually a matter of a few days to a week or two, but for very heavy leathers may run as high as 3 months. It is accomplished by placing the hides on rocking frames within vats of the tan liquor. In order to conserve on the expensive tanning materials, the process is, in effect, a countercurrent operation. The hides first come in contact with weak liquors exhausted by use in other vats, these are the so-called "tail liquors" and are the only regular discharge from the process. The first vat is discharged daily; hence the waste from the tanning process is an intermittent one. The hides move progressively to vats containing stronger and fresher solutions until the desired degree of tannage is obtained. In tanning heavy hides, the last vat may contain layers of solid tan bark placed between the hides, as well as strong tan liquor.

Despite the fact that the tannins are utilized as efficiently as possible, the waste tan liquors constitute the strongest fraction of tannery waste from the standpoint of organic pollution and biochemical oxygen demand. A process for the re-use or recovery of this material would go far toward solving the tannery waste problem to the satisfaction of both the tanners and those charged with the protection of streams.

From this point on the process differs somewhat, depending on whether heavy or light leathers are being produced. The heavy leathers are subjected to a series of operations designed to extract excess tannin and to remove some of the color imparted by the tanning materials. The combined operation is known as "bleaching" and consists of consecutive treatments in a weak solution of soda ash or other alkali, a weak solution of acid, usually sulfuric, and a final rinse with water. The quantities of chemicals used are approximately 0.75 lb of soda ash and 2 lbs of sulfuric acid per 100 lbs of hide. The bleach solutions are often made up daily and dumped at the end of the day. These waste solutions contain substantial quantities of color and biochemical oxygen demand.

Heavy leathers are then subjected to numerous finishing operations, such as treatment with oils for flexibility and the addition of salts and sugar as weighting agents. A number of mechanical operations are performed as a part of the finishing; the leather may be rolled, polished, given

artificial grain, etc. Since these operations do not produce any significant amounts of waste, they are omitted from this discussion.

The finishing treatment of light leathers, made either from thin hides or by splitting the heavier hides, begins with a thorough washing of the stock in clean water to remove the excess tanning materials. The bleaching step appears to be frequently omitted, possibly because most of these leathers are dyed. The dyeing is done in drums, which are charged with water solutions of the dyes to be applied. The desired degree of flexibility is ensured by the process known as "fat-liquoring," in which the skins are tumbled in drums with water emulsions of various oils. The exhausted solutions from these operations are discharged and contribute to the gen-

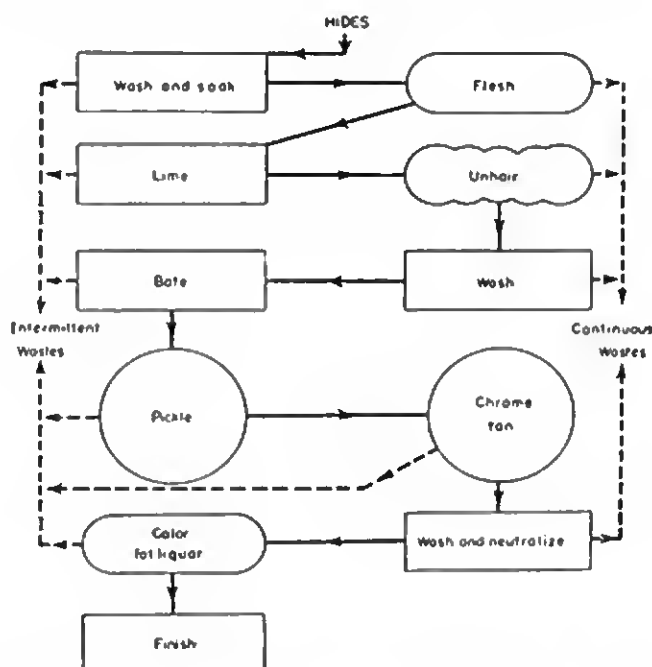


FIGURE 2. Flow sheet of the chrome tanning process

eral waste a group of colored solutions and oily emulsions not present in the wastes of a tannery concentrating on the heavier, undyed leathers. The light leathers are also subjected to a number of mechanical finishing operations, including glazing, printing with designs, and the like. Again, these processes produce no substantial amounts of waste.

Chrome Tanning

Figure 2 presents a flow sheet for the process of chrome tanning. Operations are substantially the same as for the vegetable tanning process, down to and including the "bate." Sutherland¹⁸ notes a few minor differences, such as the addition of larger quantities of sodium sulfide to the

liming solutions and a reduction in the period of liming. On the other hand, the time allotted to the "bating" operation is extended; this tends to produce a leather of greater softness and flexibility, both of which are desirable in the varieties of leather ordinarily produced by chrome tannage.

Pickling is an important step in the preparation of hides for chrome tanning and may sometimes be used prior to vegetable tanning. It consists of soaking the skins in a solution containing sulfuric acid and sodium chloride; the strengths are of the order of 0.75 per cent acid and 5 to 8 per cent salt. Pickled skins may be preserved for long periods before they are tanned. The operation is usually performed in vats, where the hides remain for 10 to 16 hours. The pickling liquors can be brought back to strength and re-used over a considerable period and are therefore discharged only occasionally.

After pickling, the skins are drained and are then put through the tanning operation. In this step, practice appears to vary considerably, but two general types of procedure may be distinguished. In the "one-bath" method, the skins are charged into drums containing a solution of basic chromic sulfate or chromic chloride produced by the addition of reducing agents to acidified solutions of sodium dichromate. Salts such as sodium chloride or sulfate may also be present to promote the penetration of the chromium salt into the skin. Tanning is completed in the rotating drum in a few hours. However, if a vat is used, it may require 2 to 3 days. Toward the end of the period, soda ash or some other alkali is added to the bath to promote the combination of the tanning agent with skin substance.

In the "two-bath" method, the skins are drummed for about 3 hours in a solution containing sodium dichromate and an acid. They are then transferred to a solution of a reducing agent, a sulfite or a thiosulfate, which reduces the chromium salt which has penetrated the fiber. Again, an alkali is added toward the end of the process to aid the action of the tanning agent. In either process the tanned skins may be held for a day or more to allow further reaction of the chromium salt with the leather. Several washes follow the tanning operation. The coloring and fat-liquoring operations are essentially the same as those applied to vegetable-tanned light leathers. The same is true of the finishing operations.

Miscellaneous Tanning Processes

There are a number of special tanning processes which warrant a brief mention. Sheepskins are often tanned with the wool left on. The liming and unhairing steps are omitted in this process and a degreasing step is substituted. The degreasing may be accomplished by treatment with

a sodium carbonate solution, which saponifies the fats, followed by a rinse, or the grease may be extracted by drumming with a petroleum solvent containing a detergent and subsequently washed in a salt solution. After degreasing, the skins are fleshed, pickled, tanned, washed, and dried by the usual methods. Either chrome or vegetable tannage may be used, depending on the final product desired. For instance, chrome tannage is used for white garments, vegetable tannage for slippers.

Chamois is produced from sheepskins by oil tannage. The preparation of the skins is much the same as that for vegetable tanning, but the skins are split before the tanning, which involves saturation with fish oils. The oil-impregnated skins are hung in drying lofts to oxidize the oils. The excess oil is then removed by washing in soda ash solution. The used soda solution is acidified to recover the oil, which commands a market as "moellen degreas" or "sod oil."

Alum is used in place of chromium salts in the production of white leathers, and many other tanning agents are used in minor quantities. These highly specialized processes have but little bearing on the question of waste disposal.

CHARACTERISTICS AND VOLUMES OF TANNERY WASTES

The composite waste from a tannery is heavy, carrying large amounts of suspended matter. The suspended matter will include such various constituents as hair, particles of flesh, and suspended particles of lime and calcium carbonate. Although the relatively high pH tends to inhibit putrefaction for a time, the waste is inherently putrescible and eventually becomes highly offensive. (Where liming of the hides is omitted, as in the tanning of sheepskins, the remarks relating to suspended lime and high pH do not apply.) One of the chief features of the waste from vegetable tanneries is the high color produced by the spent tan liquors. This approximates the natural color of water and persists for long periods in a stream receiving tannery wastes. In wastes from chrome tanneries this color is absent.

There are a few cases on record where anthrax has been transmitted to bathers or watercress gatherers through contact with tannery waste discharge to water-courses. These have all occurred in foreign countries where anthrax is more common. There are also isolated instances where arsenic, which is sometimes used in hair removal, has been present in sufficient amounts to check biological action in streams or sewage treatment plants.

One of the more annoying properties of tannery waste is its ability to form a lime mortar on the inside of a receiving sewer. This is due to con-

version of lime to calcium carbonate by the carbon dioxide produced by decomposition of the organic matter. The residual hair and fleshings act as an excellent binder. Difficulties with sewers receiving tannery wastes have been experienced in many places; the South Essex Sewerage District of Massachusetts¹³ is a well-documented example. Here one of the main trunk sewers required yearly cleaning at considerable expense, and in one year the carrying capacity of the sewer again decreased by 35 per cent within two weeks after cleaning. The sewer authority was finally compelled to prohibit discharge of caustic lime wastes, and to require treatment of the wastes with flue gas prior to discharge.

As to the total volume of tannery waste produced, the figures of Howalt and Cavett,⁸ covering 51 tanneries in various states, give a variation of from 230 to 1,790 gallons per 100 lb of hides processed per day. The bulk of these were tanneries producing sole and belting leather. The average for such tanneries is 600 to 700 gallons per 100 lb of hides per day. Tanneries producing lighter leathers and specialty products such as sheepskin tend to yield a somewhat lower volume of waste.

Composite tannery wastes vary widely in strength. Suspended solids as low as 1,500 ppm and as high as 6,000 ppm have been reported. The usual values are about 2,000 to 3,000 ppm. The 5-day biochemical oxygen demand can be as low as 700 ppm (or even less in a chrome tannery) or as high as 3,000 ppm, but usually runs 1,000 to 2,000 ppm. In vegetable tannery waste the color may be as much as 4,000 to 5,000 ppm. The quantity of dissolved solids may be several times as great as that of the suspended solids.

Analyses of the individual components of the waste are of considerable importance, since much can be accomplished in the way of treatment by segregation, individual handling, and controlled mixing of certain of the components. The outstanding study of the individual wastes from the various departments of a tannery was made by Howalt and Cavett.⁸ Their results are reproduced in part in Table 1. Values for some of the major components of vegetable and chrome tannery wastes have been collected by Sutherland¹⁸ and are given in Table 2. Another set of values, determined at a New Hampshire tannery, is given in Table 3.* They are for the production of heavy leather by the vegetable tanning process.

Analyses of wastes from a sheepskin tannery have been given by Eldridge.² For this tannery, the spent tan is notably high in strength compared to the values given in Tables 1, 2, and 3; the suspended solids run as high as 43,000 ppm, the total solids as high as 180,000 ppm, and the BOD as high as 26,000 ppm. Another feature is the presence of con-

* These figures were obtained from a thesis prepared for the author by F. J. Laiviere of the New Hampshire State Health Department.

TABLE 1. ANALYSIS OF TANNERY WASTES
Total Effluent 128,200 gals/day—617 gals per 100 lb hide tanned.
A = parts per million. B = lbs/day

Wastes	Gals./day	Total A	Solids B	Volatile A	Solids B	Suspended A	Solids B	Alkalinity† or Acidity A	Total N A	B	5-day A	BOD B
Soaks*	9,600	23,820	1,940**	2,587	211	1,888	154	689	303	24.7	558	45
		3,101	249	2,191	176	383	31	140	43	3.9	190	15
Limes*	2,900	28,764	705	4,969	122	17,003	417	28,766	1,135	27.8	3,300	80
		11,949	292	374	9	1,954	48	2,514	135	3.3	1,510	37
Hot water*	2,900	8,653	211	3,796	93	3,312	81	3,444	122	3.0	526	13
											2,255	55
Unhairing machine	3,100	1,906	49	998	26	1,102	28	751	80	2.1	140	3.6
											136	3.5
Wash wheel	25,800	1,620	349	1,096	236	448	96	224	105	22.6	502	108
Fleshing machine	7,200	3,557	214	—	—	2,517	154	112	105	6.3	462	95
Float box	4,700	276	11	—	—	146	6	28	—	—	310	19
											44	1.7
Green stock pools	43,600	385	140	250	91	94	34	112	17	6.3	6	0.3
											3	1.2
Brown hair wash	14,300	2,434	291	1,558	187	984	118	112	79	9.5	138	16
White hair wash	1,200	2,212	22	904	9	909	9	420	71	0.7	328	39
Spent tan liquor*	7,800	34,255	2,262	29,176	1,927	817	54	Acidity 1,206	89	5.9	431	4
Soda bleach*	1,700	33,720	477	25,551	359	2,983	43	Alkalinity 3,720	23	0.3	82	0.8
Acid bleach*	1,700	41,158	599	34,434	501	643	9	Acidity 18,633	58	0.8	5,725	373
											4,340	283
Acid water*	1,700	21,361	307	17,732	255	147	2	5,866	41	0.6	3,144	47
											2,715	38.5
Composite	128,200		6,342				921		41		1,700	24
											1,655	23
											1,500	21
											1,025	15
												706.4

*Intermittent Wastes.

**Largely NaCl.

†Alkalinity as CaO, Acidity as H₂SO₄.

TABLE 2. ANALYSIS OF BASIC TYPES OF TANNERY WASTES

Source of Waste	Total Solids (ppm)	Soluble Solids (ppm)	Suspended Solids (ppm)	Volatile Matter (%)	Ash (%)	BOD (ppm)	pH
Soak	15,000	13,510	1,490	1.23	0.27	1,200	6.6
Lime	26,000	18,840	7,160	1.2	1.4	2,770	11.6
Bate	4,410	4,300	110	0.32	0.12	410	8.2
Pickle	61,200	59,960	1,240	0.59	5.53	790	2.4
Vegetable tan	18,400	17,110	1,290	1.50	0.34	5,500	5.0
Chrome tan	76,800	74,810	1,990	1.58	6.10	618	3.2
Color and fat liquor	2,460	2,010	450	0.06	0.18	472	3.9

siderable grease, as much as 8,000 ppm, in the waste from the "breaks," i.e., the sodium carbonate degreasing solutions.

There are several important points to be made with respect to the individual departmental wastes of tanneries, since separation is frequently employed as a part of treatment. It will be noted that in a vegetable tannery the spent tan waste accounts for only 6 to 8 per cent of the total volume, but carries from 45 to 50 per cent of the total BOD. It also accounts for the bulk of the color found in the composite waste, although some color is present in the bleach wastes. If the spent tan can be eliminated in some manner, a long step has been taken in reducing the pollutional strength of the waste.

In the waste from a chrome tannery, the highly colored and BOD-rich vegetable tan liquor is replaced by intermittent discharges of the spent baths of mineral tanning agents. These are high in soluble, inorganic solids, low in pH value, and contain considerable chromium, mainly in the trivalent state. The chromium is moderately toxic, and can be expected to interfere with the exertion of the BOD of the composite wastes. Consequently one finds BOD values as low as 300 to 500 ppm given for composite chrome tanning wastes. It is likely that BOD determinations on this waste are of questionable validity, and that the BOD actually exerted will vary considerably with the degree of dilution of the waste. However, one may safely expect much lower values for color and suspended solids in a chrome tannery waste than those found in wastes from a vegetable tannery.

It will be noted from Tables 1 and 3 that a number of the individual waste components are relatively low in strength as for example, the wastes from the unhairing process, the hair washes, and some of the hide washes. Segregation and separate discharge of such wastes could well effect a 50 per cent reduction in the volume of wastes to be treated. Since the weaker wastes are, in general, the continuously discharged wastes and the stronger wastes are the intermittent discharges, a segregation based on this principle is feasible.

TABLE 3. ANALYSIS OF WASTES FROM A NEW HAMPSHIRE TANNERY

Operation	Gals/day	Gals/100 lb Hides per day	Total Solids (ppm)	Suspended Solids (ppm)	BOD 5-day (ppm)	Color	Population Equivalent	BOD, lb per 100 lb Hide
Soaking*	17,440	89.5	12,000	1,200	600		523	.448
Liming*	8,720	44.7	27,000	10,000	2,400		1,048	.896
Rinse*	10,900	55.8	10,500	3,500	1,000		546	.467
Unhairing	5,450	28.0	2,500	1,500	400		109	.933
Fleshing	7,530	38.6	3,500	2,600	800		302	.259
Washwheel	43,600	224.0	1,600	450	700		1,528	1.310
Spent Tan*	10,900	55.8	27,000	1,500	10,000		5,460	4.680
Bleach*	8,720	44.7	30,000	1,200	2,000		872	.747
Wash	8,400	43.1	20,000	147	1,500		630	.540
Total	121,660	624.2					11,018	10.280
Composite, Determined			9,880	3,280	1,285	4,460	7,800	6.680

*Intermittent Discharges.

WASTE RECOVERY

There are a number of possible ways in which re-use of wastes in the industry or recovery of useful by-products from the wastes can contribute toward reducing the strength of tannery discharges. Some forms of recovery are widely practiced in the industry, but many other possibilities are almost completely neglected. Both hair and fleshings are recovered to a considerable extent and marketed as by-products, but in many establishments the percentage of the total amount recovered could be greatly improved. The thoroughness of the recovery is apt to depend on the market price of the by-products; actually the process should be regarded as an essential part of waste treatment.

Recovery of grease is also widely practiced, both in sheepskin tanneries and those using the oil tanning process for chamois. Where degreasing is effected by solvents, the recovery of grease is practically complete; where degreasing is effected by solutions of alkalis, these solutions must be acidified to break the emulsion, and skimmed. This process is less efficient in eliminating grease from the waste, and may be abandoned entirely when the market value of the grease is low.

Lime sludges from the settling of spent lime solutions may occasionally be disposed of to farmers, but the return may be small or non-existent and the removal is often undependable. More effort to prepare this material in a form marketable as agricultural lime might prove profitable.

Re-use of materials within the industry itself seems to be confined to inorganic chemical solutions, that is, pickle liquors and chrome tan liquors. All attempts to recover tannins from waste vegetable tan liquors, or to re-use the spent liquors, have so far been unsuccessful, although, as Sutherland states, a solution to this problem would immeasurably simplify the waste disposal of vegetable tanneries. Waste pickle liquors are brought up to strength by the addition of the necessary chemicals, and re-used for considerable periods. Spent chrome liquors may be partially recovered by combining them with fresh liquors for re-use. Direct recovery of chromium from these liquors has been resorted to when the chromates have been in short supply. The process consists of the precipitation of chromium hydroxide by the addition of alkalis, filtration of the precipitate, and treatment of the precipitate with sulfuric acid to produce a chromic sulfate solution.

DISPOSAL OF TANNERY WASTE WITH DOMESTIC SEWAGE

Tannery waste is frequently a component of the sewage of industrial cities. In very large communities, the proportion present may be so small that no interference with sewage treatment processes is noted, even when the most sensitive forms of biological treatment are used. If the tannery

waste content does not exceed about 10 per cent of the total flow, and the tannery discharge is regular and well distributed, no difficulty with sewage treatment processes is likely to occur. As far as digestion of sludge from scwage containing vegetable tannery wastes is concerned, Warrick and Beatty²⁰ cite experiments showing that the tannery solids in the sludge can amount to as much as 40 per cent of the total solids without seriously impairing digestibility. This is not at all true of sludge derived from chrome tannery waste, which accumulates nearly all of the chromium of the waste, and may carry as much as 5 to 6 per cent ehromium on the basis of solids. Any substantial amount of chrome tannery sludge may be expected to interfere with normal sludge digestion.

In many small and moderate-size communities, tannery waste has been present in amounts sufficient to interfere with sewage treatment proccsses. The interference may be due to one or more of the following factors:

(1) Excessive alkalinity or high pH produced by the lime present in the waste, and resulting in interference with biological treatment processes.

(2) Hair and fleshings, which form scums on sedimentation tanks, clog sludge-removal equipment, or produce mats in digsters.

(3) Lime sludges and adherent deposits, which clog sewers, or interfere with proper operation of sedimentation tanks.

(4) Excessive loads of organic matter, which overload the treatment units of the plant.

Heisig and Brower⁶ reported difficulties with tannery waste in Milwaukee, chiefly through deposition in sewers. The difficulties were remedied by replacing crude lump lime with high-grade dchhydrated lime in the tannerics, by settling of the beam-house wastes before discharge to the scwers, and by the installation of stationary or rotary screens at the tanneries to remove hair and fleshings.

There are, however, a number of plants that have been designed especially for the purpose of treating scwage containing substantial proportions of tannery wastes. Hubbel¹⁰ at Rockford, Michigan, treated a mixture of 10 per cent domestic sewage and 90 per cent tannery waste by sedimentation in tanks of approximately 2 hours retention. The mixed waste had a pH value of 9.0, a 5-day BOD of over 600 ppm, and a maximum hourly suspended solids content of 1,200 ppm. No values were given for the effluent from the plant. The tanks were equipped with mechanical scrapers for sludge removal, and the sludge was dewatered on vacuum filters with the addition of 6.4 per cent of lime on the basis of dry solids. The filter eake was readily disposed of on farm land.

There is no reason to believe that mixtures of tannery wastes and domestic scwage cannot be adequately treated in properly designed

plants, provided sufficient attention is given to the peculiar properties of the waste. Provisions for the avoidance of slugs of waste in the discharge, for pH control, and for handling a sludge heavier than that obtained from normal domestic sewage should obviously be incorporated in the design. Avoidance of sludge digestion, and possibly of secondary biological treatment, is indicated if chrome tanning wastes are present in substantial quantities. Otherwise, provision of adequate capacity of the treatment units would seem to be the only requirement.

SEPARATE TREATMENT OF TANNERY WASTE

The treatment of tannery waste for disposal into watercourses usually involves one or a combination of the following techniques:

(1) Collection and storage of wastes, with regulated discharge adapted to the conditions of the watercourse. This technique may be applied to the entire waste, or it may be restricted to one or more of the concentrated waste fractions.

(2) Plain sedimentation, in basins ranging from simple earth lagoons to tanks with mechanical sludge removal. Obviously, sedimentation is also involved in (1), but it is not the primary objective, and the accumulated sludge is often discharged to the watercourse along with the wastes.

(3) Coagulation with chemicals, followed by sedimentation. Among the coagulants that have been used are alum, iron salts, and carbon dioxide in the form of flue gas, with or without the addition of lime.

(4) Biological treatment methods, including sand filters and trickling filters. Biological methods have been confined largely to pilot plant studies, mainly because of the difficulty and expense involved in treating straight tannery wastes by such methods.

Present practice in waste treatment is largely a matter of adapting one or more of the first three of the techniques cited above, as is shown by the examples from the literature which follow.

Storage and Sedimentation

The majority of tanneries which practice waste treatment of any kind have resorted to processes which are made up of various combinations of storage, sedimentation, and regulated discharge. In many instances, holding tanks are used which serve only to regulate the discharge into the stream and to extend it over a longer period of the day, making no attempt at removal of the suspended and dissolved materials. Little attention is given to sludge accumulations until it becomes necessary to remove them because the capacity of the basin is no longer adequate. In others, the weaker wastes are discharged directly and only the stronger wastes, usually the so-called intermittent wastes, are settled and subjected

to regulated discharge. Further refinements may be introduced, including selective mixing of components of the waste to produce mutual precipitation. Specific examples are given below.

Siebert¹⁷ has recommended for Pennsylvania tanneries a simple system of 3 earth lagoons, each capable of holding an entire day's flow. These are operated in rotation on the fill-and-draw principle, filling during one day and discharging over the next 24-hour period, thus leaving the third day available for sludge removal. If desired, concrete tanks

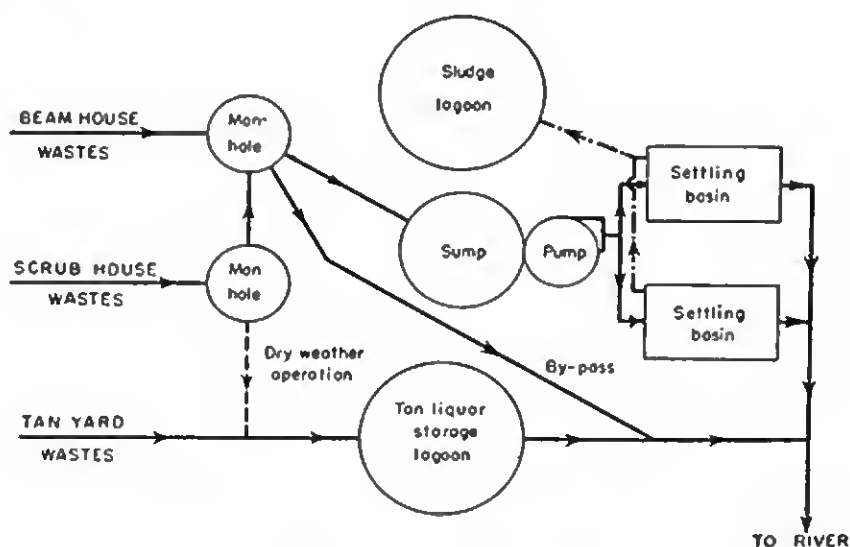


FIGURE 3. Flow diagram of tannery waste treatment plant

equipped with sludge collectors may be substituted, to avoid the labor involved in hand-cleaning the lagoons. In a system of this type, removals of 80 to 90 per cent of the suspended solids and of 40 to 50 per cent of the BOD may be expected.

To eliminate a larger portion of BOD, and to reduce the amount of color in the effluent, vegetable tan liquors may be placed in separate lagoons to be discharged only during periods of high water in the stream. The design of a treatment plant of this type has been described in detail by Reuning.¹⁴ A flow diagram is shown in Figure 3. The plant, designed for 200,000 gallons of waste per day, has 2 earthen settling basins, each of a 500,000-gallons capacity, to be operated as fill-and-draw units over a 24-hour period. The basins are provided with swing draw-off pipes for collection of effluent. Sludge will be removed by gravity flow to a storage area of large capacity. A separate lagoon for the spent tan liquors will provide storage for 200 days of normal tannery output, with controlled discharge to the stream to provide a dilution of at least 1 to 50,000. At times of very low stream flow, the "scrub house" or bleaching

wastes will also be put in the spent tan lagoon to ensure a minimum of color in the waste discharge.

A certain amount of mutual precipitation can be secured by adding the vegetable tan wastes in controlled amounts to the alkaline beam-house wastes and settling for 24 hours or more in fill-and-draw tanks. Eldridge¹ has devoted considerable attention to this process, and has developed both fill-and-draw and continuous-flow designs for it.

Harnley, Wagner, and Swope⁵ have varied the pattern by putting vegetable tan liquors through an old sludge bed for color removal by adsorption on the old sludge. The effluent is mixed with the remainder of the plant waste, the bulk of which is chrome-tan waste, and the mixture is settled in tanks equipped with mechanical sludge removal devices. The detention periods in these settling tanks have varied from 9 to 15 hours. About 83 to 88 per cent of the suspended solids have been removed from influents ranging from 800 to 1,000 ppm of suspended solids; 63 per cent of 423 ppm of BOD was removed in one series of tests, but only 40 per cent of 335 ppm was taken out in another series.

Sutherland¹⁸ has secured a reduction of 69 per cent of the suspended solids in a side-leather tannery waste (influent 1,200 ppm, effluent 370 ppm) by plain sedimentation for 2 hours. This is representative of what may be accomplished by short-period sedimentation.

Chemical Precipitation

Where the degree of treatment obtainable by plain sedimentation is insufficient, some tanneries have considered coagulation by the addition of chemicals. The coagulants that have been tried include sulfuric acid, carbon dioxide from flue gas, alum, and iron salts. Mechanical flocculation has sometimes been used as a part of the treatment. In general, the improvements observed in the effluents, as compared with those obtained by plain sedimentation, are confined to better removals of suspended solids and possibly of color. The additional BOD removals secured are often disappointing.

Alum probably has the longest history of use; it has been tried by several Massachusetts tanneries as an auxiliary to sedimentation during periods of low-stream flow. The plant of Winslow Bros. and Smith, described by Fales,³ was designed to treat the wastes from a light leather tannery, combined with a relatively small quantity of acid-cracked wool-scouring effluent (25,000 gallons in a total of 400,000 to 600,000 gallons). Under ordinary conditions, the waste was settled and discharged directly to a small stream. During periods of warm weather and low-stream flow, the effluent from the sedimentation tank was reduced by sulfuric acid to a pH value of 5.2 and coagulated with alum. The quantities of chemi-

eals used were about 2,000 lbs of sulfuric acid and 1,000 lbs of alum per 1,000,000 gallons of waste. After further sedimentation, a part of the waste was passed through sand filters, and a part discharged directly to the stream. The results obtained are fairly representative of what can be accomplished in the way of additional removals by chemical treatment, and are given in brief in Table 4. The plant was later aban-

TABLE 4. EFFICIENCY OF TREATMENT OF WASTES FROM WINSLOW BROS. AND SMITH COMPANY

Averages, June 28–October 16, 1927.
All Results in ppm

	Crude Waste	Settled Waste	Effluent after Alum and Settling	Sand Filter Effluent
Oxygen Consumed				
Total	703	344	231	66
Dissolved	259	232	192	
Suspended	444	112	39	
Suspended Solids				
Total	1,550	300	68	
Volatile	994	147	23	
Fixed	556	153	45	
Fats (ether extract)	678	195	45	19

doned when a main trunk sewer of the Boston Metropolitan Sewerage System became available for discharge of the wastes.

Howalt and Cavett⁸ also employed acid and alum on a pilot-plant scale. They mixed the intermittent wastes with air, adjusted them with sulfuric acid to a pH of 5.5, settled the acidified wastes overnight, and added the supernatant liquor from this treatment to the continuous wastes. They then coagulated the mixture with alum and passed it to a second stage of sedimentation. The quantities of chemicals used were approximately 2,300 lbs of sulfuric acid and 2,700 lbs of alum per 1,000,000 gallons of total waste. The results obtained on a waste much stronger than that of the Winslow Bros. and Smith Tannery are briefly summarized in Table 5.

TABLE 5. EXPERIMENTAL TREATMENT OF TANNERY WASTE WITH ACID AND ALUM

All Results in ppm

	Intermittent Wastes Treatment		Final Treatment	
	1. Influent	2. Effluent from Acid Treatment and Settling	3. Mixture of (2) and Continuous Wastes	4. Final Effluent after Alum and Settling
Total Solids	21,600	20,600	13,600	6,500
Suspended Solids	2,500	1,100	2,800	850
Color	12,100	5,700	3,000	850
5-Day BOD	3,800	3,400	2,000	1,030

The volumes of sludge produced in this treatment are of interest: about 11,000 gallons of sludge were secured from each 100,000 gallons of total waste treated. Of this, about 8,000 gallons were from the acid pretreatment of the 43,000 gallons of intermittent waste contained in 100,000 gallons of total waste, and the remainder developed from the alum treatment of the total mixture.

In Germany, Kunzel-Mehner¹¹ successfully treated tannery wastes with ferric chloride, using 1,670 to 4,170 lbs per 1,000,000 U.S. gallons (200 to 500 g per cubic meter). A high degree of clarification was obtained, and the objectionable sulfur compounds present in the waste, chiefly as sulfides, were completely removed. The sludge was dewatered by means of a vacuum filter, and the filter cake incinerated.

In experimental investigations, Maskey¹² secured a high degree of treatment of heavy-leather beam-house waste by carbonating to a pH value of about 6.0 and then coagulating with ferric chloride (300 to 500 ppm). Suspended solids were reduced from 6,190 ppm to 58 ppm and the BOD from 2,180 ppm to 325 ppm. The floc was heavy and quick-settling, and amounted to 10 per cent of the volume of waste treated. That such a high degree of purification could be secured in an actual treatment plant seems doubtful.

Other iron salts, such as ferric sulfate, have been used in experimental work, either alone or in conjunction with lime, but they do not seem to have been adopted for actual plant use. German workers have used iron filings plus carbonation, followed by aeration. There is no evidence that any of the other iron salts or any of the combinations are more effective than ferric chloride alone.

The use of flue gas for the elimination of caustic lime in tannery waste was practiced in Massachusetts tanneries as early as 1930, and several plants still make use of the process. The objective has been primarily the reduction of deposits on the interior of sewers. Riffenburg and Allison¹⁵ have developed a process using flue gas and lime for the treatment of the strong components of tannery waste. Their method consists of mixing the intermittent wastes in a basin holding 24 to 36 hours' flow, and bubbling in flue gas until the pH value of the mixture has been reduced to 6.4 to 6.7. Lime suspension is then added until phenolphthalein alkalinity appears, and the waste is settled for 3 hours. The supernatant is then drawn off and subjected to a second stage of treatment identical to the first. Their pilot plant, taking an influent of 13,400 ppm of BOD, 64,800 ppm of color, and 17,000 ppm of total solids, produced a first-stage effluent containing 3,000 ppm BOD and 25,850 ppm of color. The second-stage effluent had 1,140 ppm of BOD, 427 ppm of color, and 8,500 ppm total solids. The method would appear to have practical possi-

bilities, since both flue gas and lime will ordinarily be available at most tanneries.

The waste from sheepskin tanneries, as Eldridge² has shown, can be coagulated with lime to secure an increased removal of BOD and suspended solids. He recommends the use of fill-and-draw sedimentation tanks rather than continuous-flow tanks because of the rapid changes in the character of the waste. Some of the results of his pilot plant experiments are shown in Table 6.

In this waste, coagulation with lime appears to improve the removal of BOD to a greater extent than it does suspended solids. Sludge amounts to about 5 per cent of the volume of the waste.

Chlorine does not appear to have been used to any extent in the treatment of tannery wastes, although Howard⁹ has mentioned the successful use of 300 ppm of chlorine as a temporary measure to correct odor conditions due to tannery waste in a receiving stream.

Sludge Disposal

All methods of treatment of tannery wastes involving sedimentation, with or without the addition of chemicals, result in rather formidable quantities of sludge, amounting to 5 to 10 per cent of the total volume of the waste. The disposal of this sludge in an acceptable manner frequently presents a more difficult problem than does the treatment of the waste.

Probably the most common practice is to discharge the sludge to low-lying areas of waste land or to specially prepared sludge lagoons. This is feasible only if sufficient land area can be provided. A thick sludge will require a smaller area, but thick tannery sludge is notoriously difficult to pump. Mention is seldom made of drainage from sludge disposal areas, but such drainage occurs, and may in part defeat the purpose of treatment if it reaches the stream which the treatment is designed to protect. The partially dried material from these disposal areas has some fertilizing value and, in addition, contains about 10 per cent of lime. In many places it is taken by farmers as fertilizer and soil-conditioner.

A somewhat more satisfactory method of sludge disposal is the provision of drying beds of sand or cinders, with or without underdrains. The Winslow Brothers and Smith plant, described previously, had sand beds provided with skimming pipes arranged so that the top water from the beds could be drawn back into the primary sedimentation tanks. This practice is recommended by other engineers who have concerned themselves with tannery wastes. Siebert¹⁷ has recommended that beds be provided on the basis of 1 sq ft of area per lb of hide processed per day. He states that the wet sludge depth on the beds should not exceed

TABLE 6. TREATMENT OF SHEEPSKIN TANNERY WASTE

Method of Treatment	Suspended Solids		Reduction (%)		BOD		Reduction (%)
	Influent, (ppm)	Effluent, (ppm)	Influent, (ppm)	Effluent, (ppm)	Influent, (ppm)	Effluent, (ppm)	
Plain sedimentation							
Continuous flow	1184	680	43	1046	537	48	
Fill-and-draw	1880	461	67	1285	873	30	
Lime treatment							
Continuous flow, 1,400 ppm lime	918	469	46	1001	476	55	
Fill-and-draw 1,700 ppm lime	1980	497	73	1630	823	49	

TABLE 7. RESULTS OF COMPLETE TREATMENT OF TANNERY WASTE—WEIGHTED AVERAGES IN PPM
DECEMBER 1916 TO DECEMBER 1917

	Suspended Solids	Ammonia Nitrogen	Alkalinity		Biochemical Oxygen Demand		Color
			Carbonate	Bicarbonate	5-day	10-day	
Composite wastes entering plant	1718	25	653	741	1209	1578	
Effluent of coagulating and settling tank	613	25	0	—	944	1224	
Effluent of filters: cinder filter	103	9.9	0	518	149	229	192
Effluent of sand filter (fed from coke filter)	105	13.1	0	600	204	313	261
Effluent of sand filter (fed from cinder filter)	18	4.4	0	478	29	53	171
Effluent of sand filter (fed from coke filter)	18	5.4	0	551	44	78	218

2 ft, and that the sludge can be removed from the beds at a moisture content of 80 per cent.

Vacuum filters have been used in a few places for dewatering tannery sludges, but have not been particularly successful. The sludges appear to clog the filter media quite readily, and the usual sludge-conditioning chemicals do not effect much improvement. There is a possibility that inexpensive filter aids, or waste products from the tannery, such as buffer dust and shavings, might improve the filtrability of the sludge and make the use of vacuum filters practicable. A report by the Committee on Stream Pollution of the American Leather Chemist's Association¹⁹ lists one plant as using centrifuges as a temporary method of sludge dewatering.

Secondary Treatment

Treatment of tannery waste beyond the level of plain sedimentation or chemical precipitation has heretofore been seldom employed, and authorities in charge of pollution control have been reluctant to force it on the tanneries because of the great expense involved. However, it is evident from the previous discussion that some form of secondary treatment of tannery waste is necessary in situations where the degree of dilution available in the stream is small.

The fundamentals of secondary biological treatment of tannery wastes on trickling filters were worked out by Hommon⁷ as early as 1919, on the basis of fairly large-scale pilot plant studies. The final system of complete treatment as developed by Hommon consisted of the following steps:

- (1) Mixture of spent tan liquors and lime sludge followed by 24-hour sedimentation.

- (2) Treatment of the remaining mixed tannery waste, plus the effluent from step (1) with 10 grains of copperas per gallon followed by sedimentation for 4 hours.

- (3) Treatment of the effluent from (2) on trickling filters, using screened cinders or coke as medium, at rates of 0.19 to 0.3 million gallons per acre per day.

- (4) Treatment of the effluent from (3) on sand beds at rates of 0.29 to 0.43 mgad.

- (5) Drying of sludge from steps (1) and (2) on sand beds.

The results secured from an experimental plant at Cincinnati, Ohio, tannery are given in some detail in Table 7. They serve as a demonstration of what can be accomplished in the way of complete treatment of this difficult waste, assuming that the high cost of such treatment can be met. Hommon advised the use of settling tanks with a 1-hour detention period between the coarse filters and sand filters in any practical

plant design, and stated that even better results could be expected if this were done. In any case it is evident that proper secondary treatment can produce from tannery waste an effluent approximating that obtained from a plant providing complete treatment for domestic sewage, except for the residual color, which appears difficult to remove. Hommon emphasized the fertilizing value of the sludge produced in the plant; some agricultural experiments showed it to have considerable promise.

A more recent investigation by Sarber¹⁶ deals with the treatment on an experimental trickling filter of sole leather beamhouse wastes previously treated by pH reduction with acid and coagulation with ferric chloride, followed by sedimentation. The range of the strength of the influent to the filter was from 365 to 480 ppm of 5-day BOD. At a rate of application of 1.5 mgad, the effluent contained 30 to 40 ppm of BOD. As the rate of application increased, the effluent BOD increased, until at 6.0 mgad the effluent contained 68 to 83 ppm.

The Pennsylvania State Health Department has recommended single- or two-stage trickling filter treatment of tannery wastes, as well as the combination of chemical precipitation and trickling filtration described above. In general, it may be said that sufficient information is available to design secondary treatment units for tannery wastes, but that the cost of such treatment makes it relatively unattractive to the tanneries.

There are also a number of patented methods for the treatment of tannery waste, which vary all the way from simple schemes for mixing the wastes from different parts of the process in a special order or sequence, to complex treatments with cyanides, copper salts, and the like. None of these patented processes are in practical use.

In conclusion, Table 8 is presented, containing the results of a survey on tannery waste treatment made by the American Leather Chemists' Association. It serves to show, first of all, the relative simplicity of the treatment plants, and the rarity, in practice, of the more complex treatments discussed in the literature. It also gives some valuable data on the quantity of waste per day and per lb of hide discharged by representative tanneries. It shows that sludge drying and disposal methods consist primarily of drying beds or lagoons, producing dried sludge which is disposed of as fill or fertilizer. The figures given for treatment plant efficiencies are obviously on the optimistic side. Inspection of this table will show that out of 32 plants reporting, only 5 had adopted the relatively simple procedure of lagooning the spent tan liquors for discharge at periods of high-stream flow, and 1 each utilized biological filtration and chemical precipitation (lime). A survey taken today would yield substantially the same results, with perhaps one or two more plants using some form of chemical precipitation or biological filtration.

**TABLE 8. SURVEY OF TANNERY
Stream Pollution Committee**

Description of Treatment	Type of Sludge Removal	Disposal of Sludge		Plant Efficiency Red'n. from Raw Wastes in:			Discharge Location of Final Effluent
		Temporary	Permanent	Settleable Solids (%)	Suspended Solids (%)	5-Day BOD (%)	
Plain sedimentation. Basins operated as flowing-through units. Final effluent discharged at uniform rate 24 hours per day.	Mechanical	Lagoons	Fill & Fertilizer	None Given			Stream
Ditto	Hand (Gravity)	"	Lagoons	" "			"
Ditto	Mechanical	"	Fill	" "			"
Tanks used as fill and draw units. Final effluent discharge rate uncontrolled.	"	Sand Beds	Fill & Fertilizer	" "			Lake
Combined raw waste storage and mixing unit, followed by flowing-through settling unit with continuous sludge removal. Final effluent discharged over 12 hours.	"	Lagoons	Fertilizer	" "			Stream
Ditto No. 29	"	"	Fill	" "			"
Ditto No. 29	"	Sand Beds	Fill & Fertilizer	92			"
Basins operated as flowing-through units. Final effluent discharged at variable rate over 10-12 hours.	Hand	None	"	99-100			"
Basins operated as flowing-through units. Final effluent discharged normally at variable rate over 24 hours.	"	"	"	90-95			"
Two basins operated as fill and draw units. Final effluent discharged at uniform rate over 24 hours.	"	Lagoons	Lagoons	93-95	93	87	"
Collection and mechanical flocculation followed by flowing-through settling unit with continuous sludge removal and secondary sedimentation and flow-equalization. Final effluent discharged at uniform rate over 24 hours.	Mechanical	Centrifugal	Fill & Fertilizer	95-98	83	80	"
Two basins operated as fill and draw units. Effluent discharged to combined sedimentation and flow-equalization basin.	Hand	None	Fertilizer	None Given			"
Two basins operated as fill and draw units.	"	"	"	" "			"
Basins operated as flowing-through units.	"	Lagoons	Fill	" "	97	50	"
Preliminary screening followed by single mechanically cleaned flowing-through unit. Final effluent discharge rate not controlled.	Mechanical	"	Lagoons	" "			"
Flowing-through settling unit for beam house wastes with controlled discharge of final effluent over 24 hrs. Yard and scrub house wastes lagooned and discharged at controlled rates during high water periods.	Hand	None	Fill & Fertilizer	100			"
Tanks operated as fill and draw units. Controlled discharge of final effluent over 24 hrs. Spent tan liquors lagooned and released during high water.	Semi-Hand	Lagoons	"	95-98	94	88	"

WASTE TREATMENT PLANTS (Cont.)
American Leather Chemists' Association

Tannery No.	Type of Leather Manufactured	Kind of Tannage	Design Capacity of Treatment Works (Gals)	Theoretical Detention Period (Hrs)		Number Pounds of Raw Hide Per Day	Volume of Raw Wastes Per Day (Gals)	Gallons Raw Wastes Per Pound Raw Hide Per Day	Total Available Settling Capacity of Treatment Works (Gals)
				At Design Capacity	At Present Operating Schedule				
29	Heavy	Vegetable	450,000	71	105	34,000	300,000	5.8	4,000,000
30		"	600,000	31	33	46,000	550,000	12.0	2,300,000
31	"	"	250,000	37	54	25,000	170,000	6.8	1,150,000
32	"	"	300,000	9	13½	28,000	200,000 (Est.)	7.1	340,000
33	"	"	100,000	8	8½	24,000	95,000	4.0	100,000
34	"	"	140,000	80	102	16,000	110,000	6.9	1,400,000
1	"	"	225,000	8	8	35,000	225,000	6.4	225,000
2	"	"	50,000	112	110	7,000	40,000	5.7	700,000
4	"	"	270,000	59	80	30,000	200,000	6.7	2,000,000
6	"	"	250,000	19	26	30,000	185,000	6.2	600,000
8	"	"	300,000	16	19	45,000	250,000	5.6	600,000
24	"	"	300,000	133	266	15,000	150,000	10.0	5,000,000
25	"	"	275,000	4	4	58,500	275,000	4.7	141,000
26	"	Chrome & Vegetable	1,500,000	48	50	165,000	1,450,000	8.8	9,000,000
19	"	Vegetable	80,000	25	40	25,000	50,000	2.0	250,000
3	"	"	50,000	64	80	7,000	40,000	5.7	400,000
5	"	"	105,000	17	19	15,000	05,000	6.3	225,000

**TABLE 8. SURVEY OF TANNERY
Stream Pollution Committee**

Description of Treatment	Type of Sludge Removal	Disposal of Sludge		Plant Efficiency Red'n. from Raw Wastes in:			Discharge Location of Final Effluent
		Temporary	Permanent	Settleable Solids (%)	Suspended Solids (%)	5-Day BOD (%)	
Mechanical flocculation; primary and secondary sedimentation with flow-equalization to provide uniform 24 hr discharge. Spent tan liquors lagooned and released during high stream flows.	Mechanical	Lagoons	Lagoons	90-95	90	81	Stream
Screening; primary and secondary sedimentation and flow-equalization. Impounding reservoir for low water storage. Spent tan liquors lagooned and released at controlled rate during high stream stages.	"	"	Fertilizer	98-99	94	50	"
No description given.	"	"	Lagoons	97-98			"
Basins operated as flowing-through units. Discharge of final effluent regulated uniformly over 16-20 hr period.	Hand	None	Fill	None Given			"
				96	92	73	
Preliminary screening; coagulation with lime; flowing-through grit-chamber. Final effluent discharged to sewer for further treatment in city plant.	Mechanical	None	Fertilizer	None Given			City Sewer
Two tanks providing alternate fill and draw operation. Uniform discharge of final effluent over 24 hr period.	"	Drying Beds	Fill & Fertilizer	93	89	89	Stream
Basins operated as flowing-through units. Final effluent discharged at uncontrolled rate over 10-12 hrs.	Hand	Lagoons	Fill	None Given			"
No description given.	Not Given	"	Not Given	" "			City Sewer
Preliminary screening, followed by two mechanically cleaned settling units operated in parallel. Final effluent discharged at approximate rate influent received. Tan liquors decolorized by lagoon leaching; resulting liquid included with raw wastes.	Mechanical	None	Fill	" "	85	50	Lake
No description given.	"	Lagoons	Fertilizer	" "			City Sewer
Primary settling tank and two secondary settling basins operated singly or in parallel. Effluent applied to cinder and stone filter beds before discharge. Sludge dried on similar type beds.	Hand	Cinder Beds	Fill	" "			Stream
Single flowing-through settling basin. Final effluent discharged at variable rate controlled by influent flow.	Not Given	Lagoons	Fertilizer	" "			"
Single flowing-through settling unit.	" "	Sand Drying Beds	"	" "			"
Single flowing-through settling unit. Sludge removed monthly and dried on cinder beds.	Mechanical	Cinder Beds	Lagoon & Fertilizer	" "			City Sewer
				93	87	70	
Four tanks operated as two parallel flowing-through units. Final effluent discharged over 10-12 hr period.	Mechanical	Lagoons	Fertilizer	None Given			Stream

WASTE TREATMENT PLANTS
American Leather Chemists' Association

Tannery No.	Type of Leather Manufactured	Kind of Tannage	Design Capacity of Treatment Works (Gals)	Theoretical Detention Period (Hrs)		Number Pounds of Raw Hide Per Day	Volume of Raw Wastes Per Day (Gals)	Gallons Raw Wastes Per Pound Raw Hide Per Day	Total Available Settling Capacity of Treatment Works (Gals)
				At Design Capacity	At Present Operating Schedule				
7	Heavy	Vegetable	255,000	13	15	35,000	225,000	6.4	425,000
22	"	"	2,500,000	10	12	200,000	2,000,000	10.0	3,000,000
13	"	"	Not Given			12,000	60,000	5.0	Not Given
35	"	"	200,000	22	22½	25,000	195,000	7.8	550,000
AVE. RANGE			410,000	39	55	66,857	326,910	6.8	1,620,450
21	Light & Heavy	Chrome & Vegetable	Not Given			45,000	405,000 (Est.)	9.0	Not Given
9	Light	"	50,000	16	20	5,000	40,000	8.0	100,000
10	"	"	90,000	14	20	6,000	65,000	10.8	162,000
12	"	"	Not Given			Not Given	Not Given		Not Given
15	"	"	2,000,000	11½	21½	85,000	1,100,000	12.9	340,000
16	"	"	Not Given			Not Given	1,000,000		Not Given
28	"	"	65,000	10½	13½	5,000	50,000	10.0	85,000
17	"	Chrome	180,000	20	30	10,000	120,000 (Est.)	12.0 (Est.)	450,000
20	"	"	550,000	9	9	45,000	550,000	12.2	600,000
27	"	"	500,000	2	4½	12,000	250,000	20.8	135,000
AVE. RANGE			490,714	10	14	26,625	397,778	12.0	267,429
23	Heavy	Chrome	65,000	7½	7½	3,200	65,000	20.3	60,000

WASTES FROM EDIBLE OIL REFINING AND SOAP MANUFACTURE

The refining of vegetable and animal fats for the production of edible oils, margarines, or shortening agents, the hydrogenation of vegetable oils for their conversion into margarines or shortening, the production of laundry soaps from lower-grade fats, and the by-products of the edible fat refining are operations likely to be carried on in a single establishment. Even when this is not the case, the wastes produced from these operations are sufficiently similar in character to be discussed under a single heading. They consist, in the main, of emulsions of impure fats, stabilized by the soaps formed from the fats and fatty acids in the course of treatment with caustic soda, which is the essential part of both the refining process and of the manufacture of soap. Such wastes can be, and often are, extremely strong; 5-day BOD's as high as 30,000 to 50,000 ppm have been reported, although the averages are considerably lower than this.

A representative edible oil refining plant, processing cottonseed oil consists of refining, bleaching by hydrogenation, winterizing, decolorization, margarine manufacturing and shortening finishing. The "soap-stock," consisting of saponified fatty acids resulting from the caustic refining, is shipped to another plant for the manufacture of laundry soap. The worst waste produced in the operation is the wash water from the washes immediately following the caustic treatment. It amounts to about 15 per cent of the volume of the oil processed and contains 0.4 per cent soap, 1.4 per cent emulsified oil, and 0.45 per cent of other organic substances. Total solids are 2.7 per cent and the pH value is 12.0. Wastes from the other operations serve mainly to dilute this wash water. The spent decolorizing compounds are removed as solids and disposed of separately, and little or no waste is produced in the hydrogenation plant other than condensates, cooling water, and occasional washings from equipment. Slugs of alkali are discharged occasionally from hydrogen scrubbers. Oily condensates from the deodorization process are also troublesome, but they contain valuable substances such as tocopherols and Vitamin E and are often processed for recovery. In the margarine plant the wastes are derived from periodic washings of utensils, equipment, and floors.

The composite waste from a typical edible oil refining plant located in Texas was found to have an average BOD of 8,000 ppm and a pH value of 11.0 to 12.0.* It contained about 3,500 ppm of material soluble in petroleum ether, and the ratio of volatile to fixed solids was 3 to 1.

* Material relating to this plant has been taken from a thesis prepared under the direction of the author by Pope A. Lawrence, formerly of the Texas State Health Department.

Treatment with acid to recover fats, followed by sedimentation, was tried on an experimental basis, with the following results:

Effluent Composition

Total solids	5,000 ppm
Volatile solids	1,600 ppm
Fixed solids	3,400 ppm
Oxygen consumed	350 ppm
5-day BOD	1,200 ppm
pH value	2.0

A sludge volume of 10 per cent of the total waste was obtained, but only 2 per cent by weight of the sludge was recoverable fat. Since this treatment was costly and not too promising, extensive studies were made on the effect of lagooning the unacidified waste water over a long period. It was found that storage in a succession of lagoons over a period of 2 months could be expected to reduce the BOD from 8,000 ppm to 300 ppm and the pH value from 11.0 to 7.8. In subsequent tests even better reductions have been reported. The reduction was attributed primarily to sedimentation and anaerobic digestion; sunlight had a beneficial effect also. Since the plant is located in a region of low rainfall, a large lagoon system providing the necessary detention period has been adopted for treatment of the waste.

The literature on wastes from edible oil processing and soap manufacture is limited, and a large part of it relates to practice in Europe, where fat recovery is of greater importance than in this country. The wastes have interfered with the operation of sewage treatment plants, principally because of their high grease content; sludge digestion tanks and activated sludge plants are particularly susceptible to them. Efforts at treatment of the wastes seem to be confined largely to the precipitation and recovery of fats and fatty acids. Free fats, if present, are separated from the wastes by skimming. Emulsions of fats in soapy liquors are cracked with sulfuric acid to break the emulsion and sludges and scums composed in part of fatty acids and true fats are separated from the cracked liquors. The recovered materials are generally used for the manufacture of lower-grade soaps. Glaser¹ has given a brief discussion of the waste treatment works of a margarine plant using this process. He was primarily concerned with the destruction of a concrete municipal sewer by the acid-cracked waste, which had been insufficiently neutralized with lime before discharge. No revision of the treatment process was considered necessary other than a more complete neutralization of the acid liquors, cooling of hot wastes, and ventilation of the sewer to prevent formation of hydrogen sulfide from the sulfate present in the wastes.

Other proposed methods, some of which are patented, refer to the use of lime and calcium salts for precipitation of the soaps and consequent removal of the fats in scums and sludges, which are subsequently treated in various ways for recovery of fat. None of these methods have been applied in practice to any great extent. Even when war-market conditions have provided easy sale of recovered fats at high prices, the manufacturers producing fat-containing wastes have been reluctant to go beyond sedimentation and skimming methods, or at the most, some simple form of acid treatment. In this, their judgment is confirmed by the statements of many authorities on waste treatment, who have pointed out that the lure of profitable "recoveries" by elaborate processes has often hindered the development of cheap and effective methods of waste treatment. Until the resources of the world are at a much lower ebb than they are now, economical waste treatment for the protection of streams will continue to be the greater need.

References

1. Eldridge, E. F., "Industrial Waste Treatment Practice," 182-189. New York, McGraw-Hill Book Co. (1942).
2. Eldridge, E. F., *Mich. Eng. Expt. Station Bull.* **87**, 32-41, Nov. 1939.
3. Fales, A. L., *Ind. Eng. Chem.*, **21**, 216 (1929).
4. Glaser, *Gesundheits Ingenieur* **58**, 254 (1935).
5. Hanley, J. W., Wagner, F. R., and Swope, H. G., *Sewage Works J.*, **12**, 771 (1940).
6. Heisig, H. M., and Brower, J., *Sewage Works J.*, **4**, 680 (1932).
7. Hommon, H. B., "The Purification of Tannery Wastes," U.S. Public Health Bulletin No. 100. November, 1919.
8. Howalt, W., and Cavett, E. S., *Trans. Am. Soc. Civil Engrs.*, **92**, 1351 (1928).
9. Howard, N. J., *Water and Sewage (Can.)*, **85**, 11, 21 (1947).
10. Hubbell, G. E., *Water Works and Sewerage*, **82**, 331 (1935).
11. Kunzel-Mehner, A. *Gesundh. Ing.*, **66**, 300 (1943).
12. Maskey, D. F., *J. Am. Leather Chemists' Assoc.*, **36**, 121 (1941).
13. Report of the Joint Board Established for an Investigation of the Sewage Problem of the South Essex District. Commonwealth of Massachusetts House Document 1250, Nov. 28, 1934.
14. Reuning, H. T., *Sewage Works J.*, **20**, 525 (1948).
15. Riffenburg, H. B., and Allison, W. W., *Ind. Eng. Chem.*, **33**, 801 (1941).
16. Sarber, R. W., *J. Am. Leather Chemists' Assoc.*, **36**, 463 (1941).
17. Siebert, C. L., "A Digest of Industrial Waste Treatment," Pennsylvania State Dept. of Health (1940).
18. Sutherland, R., *Ind. Eng. Chem.*, **39**, 628 (1947).
19. "Tannery Waste Treatment." *J. Am. Leather Chemists' Assoc.*, **38**, 292 (1943).
20. Warriek, L. F., and Beatty, E. J., *Sewage Works J.*, **8**, 122 (1936).

9. Textile Dyeing and Finishing

Stuart E. Coburn

Metcalf and Eddy, Engineers, Boston, Mass.

The principal fibers now used in the textile industry fall into two groups: natural fibers and manufactured fibers. Natural fibers may be classified as those of animal origin represented by wool, silk, or hair; those of vegetable origin such as cotton and flax; and those of mineral origin represented by asbestos. Manufactured fibers may also be divided into two groups; the semi-synthetic, or those starting with a natural base such as rayon, and soybean or casein derivatives, and the true synthetics such as nylon, "Saran," or "Vinyon." Cotton and wool constitute 80 to 85 per cent of the mill consumption¹² of fibers today. The remainder is made up of manufactured fibers with small percentages of silk, flax, jute, and miscellaneous fibers.

In the preparation of these raw materials for spinning, weaving, and finishing, liquid wastes are produced, the volume and strength of which extend over a very wide range, depending not only on the type of fiber being processed but also on the source of the raw product, the ultimate use, availability of process water, control of manufacture, and other variables. Selection of treatment methods for these wastes will be governed by their character, the policy of the regulatory body covering the waters of the receiving stream, economics of treatment, and present-day knowledge of methods of purification.

WOOLENS AND WORSTEDS

Wool as removed from sheep contains considerable quantities of dirt, grass, burrs, excreta picked up in grazing, the dried perspiration of sheep, called "suint," and the wool grease discharged from the sebaceous glands coat which protect the fiber during the growth of the animal. Grease wool may contain as little as 30 per cent fiber and 70 per cent foreign matter, which must be removed before the fiber can be used in textile manufacture.

The wastes produced in the manufacture of woolen textiles are con-

tributed by the wool scouring, earbonizing, bleaching, dyeing, and finishing processes. All may be discharged from the same manufacturing plant, but more often wool scouring and earbonizing are done in one plant and dyeing and finishing elsewhere.

Wool Scouring

The foreign material in the wool is usually removed by scouring the wool in warm water with soap and alkali or other detergent, or by treating it with an organic solvent to remove the grease followed by a light water wash.

In either case the grease wool is first sorted into grades according to quality. It is then subjected to a mechanical process known as dusting or opening, whereby the wool is opened up ready for the scouring process. Considerable dirt, amounting to 5 to 15 per cent of the total impurities, is removed in this step and disposed of in a dry condition.

Detergent Scouring. The dusted wool is fed into the scouring machine and conveyed by moving racks through 2 to 5 bowls containing a soap and soda solution maintained at about 120 to 130°F. The first bowl may be filled with warm water only and used as a desuinting bowl. The final bowl is used for rinsing and is usually operated with a continuous flow of clean water. The wool passes between squeeze rolls at the end of each bowl where a pressure of about 3½ tons removes the dirty liquor. This liquor is settled and pumped back to the front end of each bowl. After rinsing, the wool may be carbonized, bleached, or blued before drying and going to subsequent dyeing and finishing operations.

Wool-scouring liquors are handled differently in different wool-scouring plants. Generally, the scouring liquor is pumped continuously or periodically countercurrent to the flow of wool and is removed from the first scouring bowl to centrifuges where grease and dirt are removed, the effluent from the centrifuges being returned to the second or third bowl of the scouring machine. Hoppers under the bowls, which collect sand and dirt, are discharged intermittently with some liquor to waste. Complete droppings of the scouring bowls may take place over any period of time from once a day to once or twice a week. The desuinting bowl is usually dropped daily. These wastes, together with the continuous flow from the rinse bowl, leaks and floor wash make up the source of scouring liquor wastes. Variation in operation occurs in different plants. Carbonizing, bleaching, and blueing liquors, and subsequent wash waters may be included with the above wastes to increase the volume and materially change their characteristics. A flow sheet of a typical wool-scouring process is given in Figure 1.

The volume of wastes discharged from wool scouring ranges from

1,000 gal to considerably over 4,000 gal per thousand pounds of wool scoured, depending on local conditions. The strength of these wastes is quite variable and is dependent upon the character of the raw wool, volumes of process water per pound of wool, and the extent of re-use of scouring liquor in the process. BOD will range from 2,000 to 6,000 ppm or more. Grease content may vary from 0.3 to 2.5 per cent in the scouring liquor and the suspended solids may vary from 3,000 to 30,000 ppm of which 10 to 50 per cent can be removed by sedimentation. A typical analysis of a combined wool scouring waste is given in Table 1.

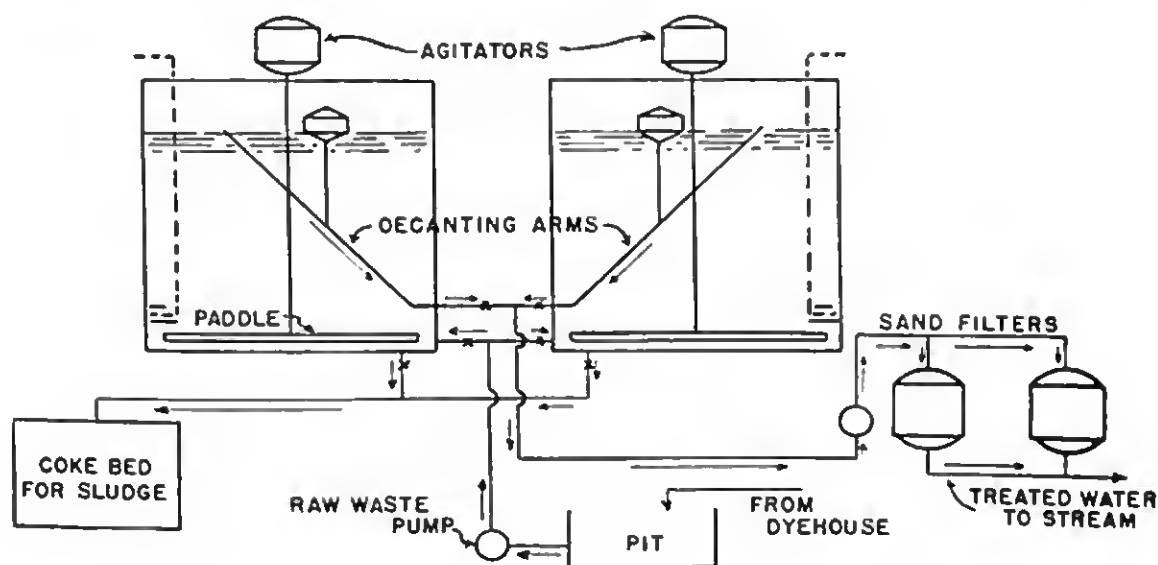


FIGURE 1. Flow sheet for batch treatment of wool scouring waste

This is an average of 5 daily composite samples, each composite being made up of catch samples collected every 15 minutes, weighted according to flow.

Treatment. Wool-scouring wastes discharged into a sewerage system would affect the treatment of sewage of a municipality in proportion to the relative volume of wastes and sewage. The types of sewage treatment plants would also be affected differently. In large cities, where the relative volume of wastes is small, the effect would be negligible provided the rapid settling solids which might cause local clogging of the sewers were first removed. In smaller communities the presence of large quantities of wool-scouring wastes would be quite objectionable to normal sewage treatment processes due to the effect of wool grease, soap, alkalis and high BOD.

Unless a sewage plant has sufficient capacity or has been designed to take the heavy load contributed by wool-scouring wastes, they should

TABLE 1. RESULTS OF ANALYSIS OF WOOL-SCOURING*
LIQUOR TREATED BY ACID CRACKING

	Scouring Liquor	Final Effluent	Per Cent Reduced
Physical Examination			
Color	dec. gray brn.	dec. buff	
Odor	dec. se. liquor	dec. se. liquor	
Suspended matter	decided	slight	
Turbidity	extreme	extreme	
Chemical Examination			
		Parts per million	
Ammonia nitrogen	48	41	14.6
Albuminoid nitrogen			
Total	145	76	47.5
Dissolved	84	64	23.8
Suspended	61	12	80.4
Residue on evaporation			
Total	21,360	13,170	38.3
Loss on ignition	13,460	5,550	53.8
Fixed residue	7,900	7,620	3.5
Suspended solids			
Total	11,940	1,510	87.5
Loss on Ignition	8,070	1,440	80.6
Fixed residue	3,870	70	98.4
pH Index			
Acidity as CaCO ₃		1,220	
Alkalinity as CaCO ₃			
Total	3,150		
Hydroxide	0		
Carbonate	560		
Bicarbonate	2,590		
Fats (Ether soluble)			
Non-acidified	7,000		
Acidified	7,600	1,820	77.1
Oxygen consumed (30 min)			
Total	7,520	2,220	71.8
Dissolved	3,400	1,600	52.9
Suspended	5,120	620	88.0
Oxygen demand, 20°			
Immediate	155	100	35.5
Biochemical, 5-day	3,315	1,680	49.4
Total	3,470	1,780	48.6

*Average of 5 daily composites collected every 15 min. over 24 hrs.

be excluded from the sewerage system. Studies at the Lawrence Experiment Station have shown that the addition of up to 2 per cent of scouring liquor to domestic sewage did not interfere with the operation of intermittent sand filters. Trickling filters have operated satisfactorily with a considerably greater proportion of wool-scouring wastes.

In general, scouring liquors should be treated at their source and the treated effluent discharged to the sewerage system or to a neighboring stream. Centrifuging, evaporation, chlorination, acid-cracking, and coagulation with calcium hypochlorite, or calcium chloride, and under certain conditions the common coagulants, alum and iron salts, have been used in treatment of these wastes. Secondary treatment can be used on effluents from the chemical treatment if stream requirements demand it.

Centrifuging. Centrifuging of wool-scouring liquors is practiced to produce an effluent which can be re-used in the scouring process with subsequent savings of water, soap, and soda or for the recovery of neutral wool fat. The centrifugal process removes from one-quarter to one-half of the fats depending chiefly on the type of wool scoured. The efficiency of the removal of grease at a typical plant is shown in Table 2.

TABLE 2

Month	Fat Content		Removal (%)
	Influent (%)	Effluent (%)	
June	0.7465	0.4600	38.5
July	0.6825	0.4870	29.5
August	0.7835	0.5375	31.2
September	1.2681	0.7615	39.8
Average	0.8700	0.5615	35.4

During this period all types of wool were scoured. This method of treatment is of little practical value for stream improvement, as the reduction of polluting matter is small. However, by re-use of the liquor, the total volume necessary to be handled by other means may be substantially reduced, thus lowering the capital costs of structures for other methods of treatment.

Evaporation. Wool-scouring wastes have been degreased and then evaporated for recovery of potash. While this method of treatment eliminates pollution of streams, the costs are prohibitive especially in plants using excessive quantities of water in the manufacturing processes.

Chlorine Treatment. Treatment of wool-scouring wastes with chlorine was suggested by De Raeve as far back as 1918. The process was patented in the United States about 1925 but has never been used commercially.

Acid-Cracking. Cracking of wool-scouring liquors with sulfuric acid and grease recovery is one of the oldest methods of treatment in continuous use.⁷

In treatment by acid-cracking the scouring liquor or "suds" receive a short period of sedimentation in a grit chamber or sand catcher to remove the quick settling solids. The liquor is then pumped to wooden

cracking tanks where sulfuric acid is added while agitating with air. The acid neutralizes the alkalies, precipitates the grease and soaps, and gives a slight excess acidity of 5,000 to 1,000 ppm.

By quiescent sedimentation the separated greases and soaps rise to the top as scum or settle as sludge carrying other finely divided suspended matter. The clarified liquor then is drawn to waste with or without neutralization. The sludge and scum are consolidated, heated and pumped to plate and frame presses where the grease is pressed out of the cake and recovered. About 50 to 60 per cent of the grease of the sludge pumped to the presses is removed, the remainder being lost in the press cake.

As an alternate method of treatment, the consolidated grease sludge in the cracking tanks may be drawn to filter beds of gravel and sand covered with a thin layer of sawdust. After remaining on these beds for several days, the partially dried sludge, known as magma, is made into cakes or puddings enclosed in pieces of burlap, in which condition it is placed upon plates in a hydraulic press and the grease removed by steaming followed by pressing.

Consideration is now being given to solvent recovery of the grease in the press cake, or to the solvent recovery of grease in the cracking tank sludge.

The sand and grit in freshly discharged wool-scouring wastes are readily settleable as indicated in Table 3.

TABLE 3

Hr Settling	Settleable Solids Removed (ppm)	Removal (%)	Settleable Solids Removed (ppm)	Removal (%)
	Liquors from light wool		Liquors from heavy wool	
0	0	0	0	0
1	3,720	62.5	29,340	73.7
3	4,560	76.3	32,540	81.
6	4,790	80.5	34,890	87.7
24	6,160	100.0	39,780	100.0

The volume of sludge removed by primary settling of scouring liquors amounts to from 2 to 8 per cent by volume of the liquor. This sludge offers a distinct problem in disposal. It is foul smelling and dries rather slowly on sludge beds because of its grease content. A practical method of disposal is to discharge this sludge to controlled lagoons and after the material is dried it can be removed by a power shovel and deposited on waste land, or used as fill.

Long periods of settling are undesirable not only on account of the rapid decomposition of the wastes and production of objectionable odors,

but also on account of the recoverable grease lost with the lighter solids which settle out when longer times are allowed for settling. On the other hand, the efficiency of treatment of hot liquors as discharged is much less than that of the treatment of the cooler liquors, and the advantage gained by quick settling may be reduced because the temperatures have not been lowered on standing. It is possible in many cases, provided cracking tank capacity is available, to pump the liquors after a short period of settling to the tanks and allow cooling to take place at this time.

The effect of temperature on the efficiency of acid-cracking is shown in Table 4.

TABLE 4

Temp. (°F)	Fats in Scouring Liquor (ppm)	Fats in Cracking Tank Efflu- ent (ppm)	Removal of Fats (%)	Acidity of Efflu- ent (ppm)
85-90	8,460	790	90.7	479
90-95	7,490	1,000	86.7	461
95-100	7,910	1,490	81.2	630
100-105	8,690	2,000	77.0	910
130	(a)5,700	2,000	64.9	1,200
	(b)15,600	6,060	61.0	

In spite of an increase in acidity of the acid wastes at the higher temperatures, the average removal is reduced from about 90 per cent at 85 to 90°F to about 65 per cent at 130°F.

The quantity of acid grease sludge to be handled ranges from 40 to 90 gals per 1,000 gals of scouring liquor. This sludge, when applied to magma beds, will drain rather rapidly and can then be made into puddings and pressed. The average composition of the dry magma and of the cake after pressing, based on numerous analyses, is shown in Table 5

TABLE 5

	Magma Before Pressing (%)	Press Cake as Discarded (%)
Moisture	53.0	23.1
Grease	36.8	17.8
Dirt	10.2	59.1
Grease-dry basis	78.3	23.7
Dirt-dry basis	21.7	76.3

The press cake from the pressing of grease sludge may be deposited on waste land. The crude grease pressed out of the grease sludge still contains considerable dirt and excess water. This is refined by adding some water

heating with live steam, adding sulfuric acid, agitating and decanting. An analysis of the crude grease and the refined oil appears in Table 6.

TABLE 6

	Crude Grease	Refined Grease
	(%)	(%)
Moisture	18.5	3.5
Grease	75.5	95.9
Dirt	6.0	0.6

Table 7 presents a summary of average operational data from an acid-cracking plant, scouring 20,000 lbs of wool per day.

TABLE 7

	Per Day
Scouring liquor treated	30,000 gal
Sedimentation tank sludge	750 gal
Acid required for cracking	1,360 lb
Grease sludge produced	2,000 gal
Magma for pressing	3.3 cu yd
Crude grease from press	1,350 lb
Refined grease	1,000 lb

Operating costs of an acid-treatment plant for wool-scouring wastes vary with type of wool being scoured, the grease content and the market prices received for the acid dégras. Under normal operating conditions the return from grease sales is usually insufficient to pay operating expenses, but under conditions such as existed during both World Wars a substantial profit was made over operating expenses.

Calcium Hypochlorite Process. A process for the treatment of wool-scouring wastes with calcium hypochlorite has been developed and used by the Fields Point Mfg. Corp. of Providence, R.I. This process consists essentially of adding to the warm wastes as discharged sufficient calcium hypochlorite to reduce the pH to about 7.5, causing coagulation and separation of the wool grease and some other colloidal and suspended solids. After 8 hours of quiescent sedimentation the clarified liquor between the deposited sludge and layer of scum is drawn to waste. The remaining sludge and scum are thoroughly mixed by agitation and sulfuric acid is added until the pH is reduced to between 4 and 5. The treated sludge is reduced about 50 per cent in volume by sedimentation and the supernatant after compaction is drawn to waste. The concentrated sludge is heated with steam to 180°F and pressed in plate and frame presses as described under acid-cracking treatment, and the recovered grease is handled in the same manner.

The average results of analyses of composite samples of wool-scouring wastes and effluents taken from a pilot plant using calcium hypochlorite as a coagulant are given in Table 8.

TABLE 8. RESULTS OF ANALYSES OF COMPOSITE SAMPLES OF WOOL-SCOURING WASTES AND EFFLUENTS FROM CALCIUM HYPOCHLORITE TREATMENT

	Wool Scouring Waste	Effluent from Hypochlorite Treatment	Effluent from Acid Treatment	Press Liquor	Com- bined Efflu- ent	Reduc- tion, (%)
Proportionate Volume (%)	100	80	10	10	100	
Parts per million						
Residue on evaporation						
Total	24,100	13,120	17,290	7,860	13,030	46.2
Loss on ignition	14,380	4,610	6,490	3,960	4,710	70.4
Fixed residue	9,720	8,510	10,800	3,900	8,290	14.7
Settleable solids—2 hr						
Total	3,020	49	335	522	122	96.2
Loss on ignition	430	29	62	367	65	85.0
Fixed residue	2,590	20	273	155	57	98.0
Alkalinity as CaCO ₃						
Carbonate	1,500	0			0	
Bicarbonate	2,300	2,100			1,320	
Total	3,800	2,100			1,320	65.4
Acidity as CaCO ₃			3,040	507		
pH Index	9.3	7.4	3.1	4.2	6.7	
Oxygen consumed—30 min	3,390	1,080	1,245	573	1,050	69.1
Oxygen demand						
Immediate	30	0	15	0		
5 days—20°C	1,770	1,000	1,470	930	1,040	41.2
Fats (acidified)	7,130	1,150	163	945	1,025	86.4

These wastes were produced from the scouring of Australian wool having a shrinkage of approximately 50 per cent.

The strength of the combined effluent was determined by weighting the analysis according to volume discharged from each step. This combined effluent had a decided amber color, a slight turbidity, and a small quantity of settleable solids, and a distinct pungent odor.

The biochemical oxygen demand of the effluent was reduced 40 per cent to about 1,000 ppm. The residual demand was due to the soluble substances not removed by precipitation and not oxidized by the chemicals. In cases where the initial biochemical oxygen demand of the wastes was much higher the percentage reduction was increased but the residual remaining in the effluent was still 1,000 to 1,200 ppm.

A summary of the operation data of pilot plant tests applied to a plant scouring 20,000 lb of wool is given in Table 9

TABLE 9

Scouring liquor treated	30,000 gal
Calcium hypochlorite solution, gal	1,050 gal
Weight of available chlorine in calcium hypochlorite	780 lb
Weight of sulfuric acid used	900 lb

It is impossible to make more than a general statement as to the economics of the process as insufficient data are available at this time. Under the high prices prevailing for grease during World War II there is little question that the return from grease sales would pay for the operating expenses of a plant.

Secondary Treatment of Calcium Hypochlorite Effluent. The combined effluent from the calcium hypochlorite process is amenable to biological treatment if it is necessary to further reduce the organic load before discharge into the receiving waters.

The results obtained on a pilot plant high-rate trickling filter operating at a rate of 15 mgad (million gallons per acre per day) on a mixture of one volume of the effluent from the hypochlorite process and 9 volumes of recirculated trickling filter effluent are given in Table 10. As shown by the table the biochemical oxygen demand of the effluent is still as great as in strong sewage.

Calcium Chloride Process. The chemical treatment of wool-scouring wastes with calcium chloride, milk of lime or other calcium compounds has been tried in the laboratory for over 50 years. The resulting sludge from such treatment, amounting in some cases to nearly one-half the volume of the original wastes, has been the principal reason why this treatment has not been used on a commercial scale.

McCarthy⁴ describes a modification of calcium chloride precipitation whereby the wool-scouring wastes were treated with carbon dioxide from stack gases or other sources to reduce the pH to below 8 after addition of the chemical. The resulting sludge is much smaller in volume, more compact and can be handled after conditioning with sulfuric acid in plate and frame presses for removal of the grease. The coagulation of wool fats and soaps is produced principally by the calcium ion as is probably the case in the calcium hypochlorite process and the effluent is similar in physical and chemical characteristics.

No full-size plants have been constructed using this process. However, a number of pilot plant tests have been conducted which show the purification that may be expected, and furnish basic data for design of full-scale plants. The results obtained from comparative tests in which the separated solids were removed by both sedimentation and flotation are given in Table 11.

TABLE 10. HIGH-RATE TRICKLING FILTER AVERAGE OF WEEKLY ANALYSES OF PILOT PLANT TESTS* ON EFFLUENT FROM CALCIUM HYPOCHLORITE PROCESS

Determination	Wool Scouring Wastes	Calcium Hypo- chlorite Effluent	High-rate Trickling Filter Effluent**	Reduction	
				by Chemical Treatment	by Chemical Treatment and Fil- tration
Physical Examination					
Color	dec. brn. gray	dec. amber	dist. amber		
Odor	dec. sc. liq.	sl. pungent	sl. disagreeable	96	98
Turbidity (ppm)	5,000	217	114 Parts per million		
Chemical Examination					
Suspended solids (ppm)	8,900	214	55	88	99
Settling solids—2 hr (%)	3.2	0.2	trace	94	100
pH	9.3	5.6	7.4		
Fats (ether soluble) (ppm)	3,800	87	19	98	99
Nitrite nitrogen (ppm)	0.0		0.2		
Nitrate nitrogen (ppm)	0.0	31.3	27.0		
Dissolved oxygen (ppm)	0.0	0.0	3.1		
BOD—5 day, 20° (ppm)	2,220	766	314	66	86

*Filter operated at 15 mgad, including 1.5 mgad chemical effluent and 13.5 mgad recirculated filter effluent.

**After passing through secondary settling tank.

TABLE 11. RESULTS OF ANALYSES OF COMPOSITE SAMPLES OF SCOURING LIQUOR AND PILOT PLANT EFFLUENTS USING CALCIUM CHLORIDE

Sample	Scouring Liquor	Sedimen- tation Efflu- ent	Flota- tion Efflu- ent	Reduction (%)	
				by Sedimen- tation	by Flota- tion
Physical Examination*					
Color	brn. 4	amber 4	amber 4		
Odor	wool scouring	wool scouring	wool scouring		
	4	4	4		
Suspended matter	3	2	3		
Turbidity	5	3	3		
Chemical Examination**					
pH Index	9.6	8.1	7.8		
Alkalinity as CaCO ₃					
Total	2,500	1,650	1,600	34.0	36.0
Carbonate	1,300	0	0		
Bicarbonate	1,200	1,650	1,600		
Chlorides as Cl	260	5,000	8,500		
Residue on Evaporation					
Total	17,595	13,350	19,610	24.1	-11.4
Loss on ignition	9,240	4,320	4,170	53.2	54.9
Fixed residue	12,355	9,030	15,440	26.9	-24.9
Suspended Solids					
Total	6,610	38	82	99.4	98.8
Loss on ignition	2,425	30	59	98.8	97.6
Fixed residue	4,185	8	23	99.9	99.4
Settleable Solids					
% by volume—2 hr.	4.2	trace	0.1	99.0†	99.0
Grease (hexane sol.)					
Total	3,370	16	15	99.5	99.5
Nonsettleable		11	12	99.7†	99.6†
Oxygen Consumed					
Total	1,600	840	980	47.6	38.8
Nonsettleable		800	900	50.0†	43.6†
BOD (5-day 20°C)					
Total	2,140	365	335	82.9	84.3
Nonsettleable		325	313	84.8†	85.4†

*These figures signify as follows: 1 = very slight; 2 = slight; 3 = distinct; 4 = decided; 5 = extreme.

**All chemical results in parts per million except pH and settleable solids.

†Percent removal if sedimentation were 100% efficient.

In these tests the sludge produced was acidified, top water decanted, and the grease recovered with plate and frame presses. The average quantity of sludge produced was 334 gals per 1,000 gals of scouring liquor. This sludge contained considerable entrained air and when it was removed the volume was reduced to 222 gals per 1,000 gals. Acidification with sul-

furic acid further reduced the volume to 70 gals per 1,000 gals of scouring liquors treated.

Solvent Scouring. In solvent scouring the raw wool is opened and dusted as for detergent scouring. It is then treated in closed containers in batches or continuously with trichloroethylene or other organic solvents to remove the grease. The solvent is redistilled, returned to the process, and the grease recovered. The degreased wool is then subjected to a light detergent-wash to remove the remaining impurities.

The detergent-wash may contain 50 per cent of the solid impurities, about 5 to 10 per cent of the grease, and 60 to 75 per cent of the BOD. These wastes may not be satisfactory to discharge into a stream, but are amenable to biological treatment.

Costs of Treatment

The total operating costs for the various methods vary widely depending on local conditions such as costs of labor, power and return from the sale of recovered grease. The cost of chemicals, however, makes up a substantial part of the operating expenses and a comparison for the three methods of treatment per 1,000 gallons of scouring liquor treated on the basis of chemicals required is of some value for cost calculations. However, the quantities of chemicals vary with the strength of the scouring liquor, and as the tests were not made on the same scouring liquors, but on liquors that were from wools with approximately the same shrinkages, the following figures (Table 12) should be used with caution:

TABLE 12. COMPARATIVE AMOUNTS OF CHEMICALS
(Per 1,000 gallons scouring liquor)

Method of Treatment	Acid-cracking	Calcium Hypochlorite Treatment (Lbs)	Calcium Chloride Treatment (Lbs)
Sulfuric acid	77	30	34
Calcium hypochlorite		26	
Calcium chloride (flake)			90

Digestion. Pilot plant experiments⁹ on anaerobic digestion of wool-scouring wastes, containing an average of 28,000 ppm volatile matter, including 11,000 ppm grease, and a BOD of 10,000 ppm, allowed a loading of 0.06 lb (dry volatile solids) per cu ft a day. The gas yield amounted to 8.6 to 14 cu ft per lb volatile matter added with a volatile matter reduction of 65 per cent and a grease reduction of 96 per cent.

Continuous Flow Treatment

In continuous flow plants the separate devices provided for each step in the treatment include equalization tanks, chemical feed machines, flash

mixers, flocculators, settling tanks, and sludge handling and disposal equipment.² When coagulated and settled waste liquor requires further treatment before discharge, it is either filtered through a mechanical filter of the rapid-sand filter type or a biological trickling filter. Means for chlorination are sometimes provided. The plant shown in Figure 2 treats

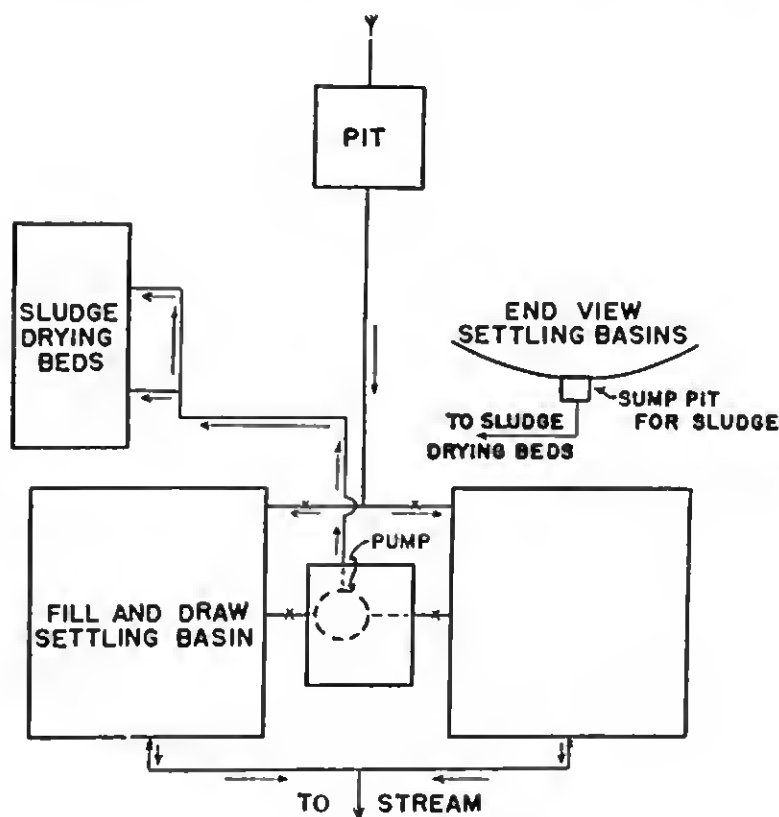


FIGURE 2. Flow sheet for continuous waste treatment

the waste from cotton kiering, dyeing, printing and finishing. The quantities of chemicals used are 5 lbs alum, 2 lbs of lime and 2 lbs of chlorine per 1,000 gals of waste.

Dyeing and Finishing

Seoured wool may be dyed in the form of "tops" or dyed and finished after spinning and weaving.

The wastes produced from the dyeing and finishing processes are contributed by the spent liquors and subsequent washings after singeing, bleaching, dyeing, and finishing. It is usually impractical to separate the rinse or wash waters from the stronger wastes within the plant, and these are collected in a common drain for treatment. There are isolated cases where cleaner waters, such as cooling and condenser waters, can be re-used in other processes or discharged directly to waste. The quantity of wastes

varies greatly, with a mean volume of about 40 gals per yard of piece goods, or about 10 gals per pound of "tops."

These wastes also vary greatly in strength, not only on account of the quantity of process water used by the different plants, but also because of the various types of dyes and other chemicals used in the finishing processes. Typical analyses of weighted composite samples of waste from top dyeing and piece goods dyeing and finishing are given in Table 13.

Wastes from wool dyeing and finishing wastes have been treated by chemical precipitation with alum or iron salts, followed by sedimentation. The effluent produced is often satisfactory for direct discharge to water courses. Filtration of the effluent on trickling filters or sand filters can be carried out if greater purification is required.

The efficiency of treatment of a wool blanket mill wastes by coagulation and filtration is shown in Table 14. In this case the combined wastes are treated with ferric sulfate settled for about 8 hrs, and the chemical effluent applied to sand beds at a rate of 110,000 gal (gallons per acre per day). The sludge is drawn by gravity to sludge beds, and when dry, removed to waste land. The final effluent is consistently of high quantity and is discharged without objection into a small brook.

Biological Treatment. The average polluting constituents (including rinse water) of wool dyeing wastes for a number of mills are given by McCarthy⁵ per 100 lbs of wool dyed as follows: total dissolved solids 0.53, volatile dissolved solids 0.18, total suspended solids 0.085, volatile suspended solids 0.026, alkalinity 0.31, fats 0.056, and 5-day BOD 0.47.

The volume of water used in rinsing usually varies from 2 to 3 times the volume used in the original dye bath. Most mills use the same drains for strong wastes, rinse waters and domestic sewage. Treatment by sedimentation and coagulation is not a satisfactory method.

Biological treatment on experimental trickling filters of the mixed wastes with small amounts of domestic sewage indicated a loading limit of about 1,000 lbs of BOD per acre foot. Recirculation increased the maximum permissible loading only by a comparatively small degree. With an average loading of about 1,270 lbs of BOD per acre foot, the BOD reduction amounted to nearly 80 per cent, leaving about 94 ppm BOD in the effluent. The sludge production from this treatment is low in volume and can be disposed of readily.

COTTON

Impurities in loose cotton fibers such as dirt, sand, and parts of the cotton plant are removed before opening and weaving. This is a dry process and presents no problem in industrial wastes treatment. The natural waxes, fats, and coloring which remain in the fiber must be re-

TABLE 13. ANALYSES OF WEIGHTED COMPOSITE SAMPLES OF WOOLEN MILL WASTES

	Top Dye House Wastes			Plant Combined Wastes (100%)	Piece Goods Wastes	
	Plant A		Plant C			
	Dye Wastes (15%)	Wash Waters (85%)			Dye Wastes	Wet Finish
Physical examination						
Color*	red-grn. 4	yel.-grn. 3	red-grn. 3	red-brn. 3	grn.-brn. 4	white 4
Odor*	soapy 3	soapy 2	soapy 3	acetic acid 3	soapy sulfide	aromatic 3
Suspended matter*	1	1	1	trace	2	3
Turbidity (ppm)	18	30	28	20	64	775
Chemical examination						
Residue on evaporation						
Total	3,320	2,152	2,327	1,548	1,355	920
Loss on ignition	970	683	725	617	345	648
Fixed residue	2,350	1,469	1,602	900	1,010	272
Suspended solids						
Total	13	18	17	trace	66	252
Loss on ignition	10	12	12		48	198
Fixed residue	3	6	5		18	54
pH index	4.9	5.5	5.2	5.1	4.8	5.3
Alkalinity as CaCO ₃ Bicarbonate	557	370	398	400	95	56
Oxygen consumed						
Total	233	160	171	705	60	350
BOD (5-day)	535	453	465	415	188	588
Fats						
Ethel sol.	28	8	11	675	42	310
Chromium as Cr.				20.8		

*These figures signify as follows: 1 = very slight; 2 = slight; 3 = distinct; 4 = decided; 5 = extreme.

TABLE 14. EFFICIENCY OF TREATMENT OF WOOL BLANKET MILL WASTES BY CHEMICAL PRECIPITATION AND SAND FILTRATION

	Combined Wastes	Chemical Treatment Effluent	Sand Filter Effluent	Removal (%)	
				by Chemical Treatment	by Chemical Treatment and Filtration
Physical examination					
Color*	gray 3	gray 2	none		
Odor*	resinous 3	resinous 2	sweet 1		
Suspended matter*	4	1	none		
Turbidity*	4	2	none		
Chemical examination					
Albuminoid nitrogen	6.5	5.5	4.5	15	31
Ammonia nitrogen	45.0	40.0	22.5	11	50
Nitrite nitrogen	none	none	0.02		
Nitrate nitrogen	none	none	1.6		
pH Index	8.7	4.3	4.3		
Alkalinity as CaCO ₃					
carbonate	127	0	0		
bicarbonate	61	6	5		
Total	191	6	5		
Suspended solids					
Total	333	32	0	90	100
Loss on ignition	301	27	0	85	100
Fixed residue	32	5	0	92	100
Oxygen consumed					
Total	294	94	36	20	88
Dissolved	159	81	36	47	77
Suspended	135	10	0	93	100
Relative Stability (%)					

*These figures signify as follows: 1 = very slight; 2 = slight; 3 = distinct; 4 = decided; 5 = extreme.

moved from the loose cotton or from the yarn or fabric. The removal of these substances involve scouring, singeing, bleaching, dyeing, starching, mercerizing, printing, and finishing, all of which processes produce liquid wastes which contain the polluting matter discharged by this industry. There are various methods of processing cotton, using two or more of the above processes depending upon the final use of the material.

Bleachery Wastes

"Bleaching" of cotton is a term loosely used in the textile industry and consists not only of whitening the cotton, but also in removing the undesirable waxes, oil, color, and nitrogenous matter, either indigenous to the cotton, or which have been added to assist fabrication, and which must be removed in the production of white goods, or goods which may be dyed in pastel colors.

Cotton may be bleached in the form of loose cotton, yarn or fabric. The types of bleaching are varied, and the method chosen in a plant depends not only on the form of the cotton, the weight of goods, the subsequent use, but also on the policies of the manufacturer.

Details of the numerous methods cannot be described here. In general, cotton is prepared for bleaching by boiling the material in open or pressure kiers in a caustic soda solution, although other alkalis are also used. This boil, with the subsequent washes, removes waxes and other impurities before bleaching. Chlorine is used in some form chiefly as the bleaching agent, although the use of hydrogen peroxide is increasing steadily, and the time required for bleaching is being gradually reduced from a matter of days to a few hours.

A typical procedure for bleaching cotton fabrics may be described as follows: Woven cotton containing the waxes, organic matter, and natural color, appropriately called "gray goods" is received from the loom in bales made up of pieces 60 to 100 yards in length. These bales are opened and pieces of the same weight and construction are marked and sewed together in the form of a rope. The heavy nap on the cotton is removed by running the goods in open form through singers where the nap is burned off. The cloth is immediately wetted to prevent a fire hazard, and then passed through a diastatic bath to desize fabrics or soften the cotton nap. The cloth is then stored or piled for a sufficient period of time to complete the breakdown of the starch and then it is washed and sent to the kiers where it is boiled.

The type of boil used also depends upon the weight of goods and their subsequent use. In single kier operation the goods are boiled for 6 to 8 hours and upon completion of this cycle the hot alkaline wastes containing a considerable proportion of the foreign matter are discharged to the waste drain. The cloth is cooled and partially washed with running water in the kier, after which it is removed and again washed in running water, "soured" in dilute sulfuric acid and allowed to lie in a pile or bin. Later the cloth is removed from the bin, again washed in running water, and passed through the "chemic" or bleaching agent, such as sodium hypochlorite solution. It is again piled to complete the bleaching reaction after which it is washed and discharged to the "white bins" for storage until ready for the finishing or dyeing operation. At times a "white" sour may be used after chemic followed by a wash before discharge to the white bins. Heavy goods may be returned to the kiers for a second boil after washing and souring.

An example of the quality of wastes produced is shown by the analyses of the wastes discharged from the steps in a double boil, processing 12,664 yds of 1.45-lb material, reported in Table 15. The volume of wastes were

TABLE 15. ANALYSES OF COMPOSITE SAMPLES OF COTTON BLEACHERY WASTES

Process	Vol. (gals)	Observations*		Turbid- ity	Oxygen Con- sumed (ppm)	Sus- pended Sol- ids (ppm)	Alkalinity as CaCO ₃		Acidity as CaCO ₃ (ppm)
		Color	Odor				Hydroxide (ppm)	Carbo- nate (ppm)	
Wet out	6,300	yel. 3	Caustic 3	3	255	76			33
1st kier boil	8,000	brn. 4	Caustic 4	4	12,300	74	2,325	3,300	5,625
Kier wash	6,800	brn. 4	Caustic 3	2	2,470	48	580	950	1,530
Wash after 1st boil	27,400	yel.-gray 3	Caustic 2	4	158	135		8	52
Wash after brn. sour	17,300	yel.-gray 3	Musty 3	3	53	22			19
2nd kier boil	8,000	red-brn. 4	Caustic 4	2	2,090	52	4,760	1,655	6,715
Kier wash	7,000	yel.-brn. 4	Caustic 3	2	1,070	55	2,590	1,070	3,660
Wash after 2nd boil	18,200	gray-yel. 3	Musty 2	2	55	38			30
Wash after white sour	11,700	yel. 2	Musty 2	3	27	9			110
Wash after ehemic	28,400	yel. 1	Chlorine 2	3	24	5			
Wash after neutralizer	22,300	yel. 1	Musty 3	3	20	7			
Total	161,400								

*These figures signify as follows: 1 = very slight; 2 = slight; 3 = distinct; 4 = decided; 5 = extreme.

measured by weirs and samples taken over 5-minute intervals to make each composite. The process water was plentiful and washers were operated at the rate of 230 yds a minute.

In another plant where process water was not as plentiful, the kier blowdown and kier wash were collected and analyzed separately from the wash waters collected from the sours and chemic. The results are shown in Table 16.

The question of separation of the strong kier wastes from the wash waters prior to treatment is problematic and must be decided in each bleachery. Factors that influence the decision are the type of bleaching

TABLE 16. ANALYSES OF COMPOSITE SAMPLES OF BLEACHERY WASTES-SINGLE BOIL

Constituent	Kier Wastes	Washer Wastes
Physical Observations		
Color	dec. brown	dist. gray-brown
Odor	dec. caustic	dist. soapy
Suspended matter	slight	distinct
Turbidity	decided	distinct
Chemical Examination	Parts per million	
Residue on evaporation	7,915	1,340
Loss on ignition	4,650	828
Suspended solids	112	86
Loss on ignition	70	84
Oxygen consumed—30 min.	4,480	470
BOD—5 day	2,120	295
Alkalinity		
Bicarbonate	none	240
Carbonate	685	none
Hydroxide	565	none
Total	1,250	240
pH Index	11.9	6.3

done, the relative strength of the wastes, the possibility of interchanging washers for other purposes, as well as the economics and engineering difficulties. In some cases heat exchangers have been used successfully to recover heat units from the kier liquors discharged.

Bleaching wastes usually may best be handled by storage and gradual discharge into the combined wastes from other finishing and dyeing operations.

Chemical treatment of cotton printing and finishing waste on a pilot plant scale,¹ consisting of equalization, coagulation and sedimentation, reduced turbidity 42.8 per cent, alkalinity 43.5 per cent, suspended solids 37.2 and BOD 45.2 per cent, using an average of 1,780 lbs of alum per million gals. The quantity of sludge produced averaged 4 per cent by volume with a dry solids concentration of 1 per cent. Compaction of sludge

for 24 hours reduced the sludge volume to 19,000 gals per million gals of waste.

Biological treatment requires fortification by N and P. Short time experiments with a high rate trickling filter¹ and a recirculation ratio of about 4 to 1 indicate that more than 50 per cent of the suspended solids and over 60 per cent BOD reduction can be expected, provided that combined wastes are conditioned with H_2SO_4 prior to application to the filter.

The suspended solids discharged from the filter do not readily settle, but amount to only about 100 gals per million gals of waste.

SILK AND SYNTHETIC FIBERS

Silk

New and greatly improved synthetic fibers such as viscose, cellulose acetate, nylon, etc., have largely replaced the natural silk fiber.¹³ Wastes from silk are mainly from degumming the raw material. The natural gum (sericin) is removed by boiling silk in a series of soap solutions and then washing. The proportion of the gum removed and hence the strength of the waste varies with the purpose for which the silk is required.^{3,10} The soap solutions used in degumming are often supplemented with sodium carbonate, sodium silicate, or sodium phosphate. Wastes from silk degumming are thick, brown, soapy, jelly-like, and putrescible.

The volume and characteristics of the waste are: 850 gallons per 1,000 lbs of silk; total solids 4,000 ppm, volatile solids 3,000 ppm, BOD, 900 ppm, population equivalent 40 per 100 lbs of goods.

Wastes liquors from the weighing of silk contain salts of heavy metals, including iron, lead and tin, which are often recovered by the use of activated alumina or ion-exchange resins.

Viscose Rayon

Of the three main production methods for rayon, viscose is the largest, cellulose acetate second and the cuprammonium process third.

In the viscose process, α -cellulose of wood pulp or cotton linters is converted to cellulose xanthate by treatment with strong caustic and carbon disulfide. The xanthate is dissolved in dilute caustic soda. A spinning solution is formed which is forced through orifices into a coagulating bath containing H_2SO_4 , $ZnSO_4$, Na_2SO_4 and glucose. The rayon is washed, spun, desulfurized with sodium sulfide solution, bleached and washed with water, dilute acid and dilute soap solution.

The principal waste is NaOH which is mostly recovered by dialysis and reused. The following ranges of characteristics of viscose waste have been reported¹⁴: 2,000 to 5,000 gals per 100 lbs rayon produced, BOD 20 to 500 ppm, total solids 500 to 5,000 ppm, acidity 25 to 2,000 ppm.

The wastes can be treated on biological trickling filters. Some average results obtained with waste washings after desulfurizing are shown in Table 17.

TABLE 17

	Raw	Effluent
pH	10.4	7.8
BOD (ppm)	700	220
Susp. solids (ppm)	68	19
Sulfides as S (ppm)	271	0
Thiosulfate, as S (ppm)	0	99
Sulfate, as S (ppm)	47	219

Roetman,⁸ reporting on treatment of washings from desulfurizing on 6-foot deep recirculating filters, states that for effluent operation an application of 300 lbs BOD per acre foot was possible when the pH of the liquor was 10.5. The loading could be increased to 1,050 lbs of BOD per acre foot, producing an effluent with 30 ppm BOD

Cellulose Acetate Rayon

Cellulose acetate is prepared from cotton linters which are first treated with soda ash solution, resembling Kiering of cotton and the waste produced is similar to spent Kier liquor. The purified cotton is treated with sulfuric, acetic acids and acetic anhydride. The acids are largely recovered and the acetate is washed with water producing an acidic waste. The two main wastes, the alkaline Kier liquor and washings, and the acidic washings, are treated in combination. The composition of a mixture of the two depends upon the proportion of Kier liquors recovered for soda by evaporation and incineration.

Cuprammonium Rayon

Rayon is produced by purifying cotton linters with caustic soda and soda ash and then dissolving in an ammoniacal solution of cupric oxide. The wastes are of relatively little importance because recovery of acids, alkalies and copper is widely practiced.

Synthetic Fibers

Synthetics such as nylon and vinyon should properly be classified in the chemical industry.¹¹ The manufacture of synthetic fibers is, in many respects, similar to the production of plastics. The wastes from plastics manufacture have, in some cases, been treated biologically after neutralization.

FLAX

The common method of obtaining fiber from flax plants is by "retting," which loosens the bundles of fiber. In the anaerobic or tank retting the flax is packed into closed, insulated concrete tanks and covered with warm water. After standing for several hours, the "leach liquor" is discharged and replaced with fresh water. During the retting period, some of the "retting liquor" is again replaced by fresh warm water. At the end of the retting the remaining dark brown, smelly liquid is discharged. The leach liquor has a BOD of about 1,100 to 1,200 ppm and the retting liquor about 2,000 to 2,200 ppm. The liquor can be treated on trickling filters, producing effluents having BOD values of 120 to 370 ppm.

Studies made by the Department of Scientific and Industrial Research Board^{6,15} resulted in a method of retting with aeration. Aeration changes the chemical characteristics of the liquor. Retting takes place under anaerobic conditions, but the destruction of organic material produced occurs under aerobic conditions so that the end product is mainly CO₂ rather than organic acids. No retting liquor is discharged until the end of the season.

References

1. Coburn, S. E., *Ind. Eng. Chem.*, **42**, 621-25 (1950)
2. Geyer, J. C., *Ind. Eng. Chem.*, **39**, 653-56 (1947).
3. Geyer, J. C., and Perry, W. A., The Textile Foundation, Inc. Washington, D.C. (1936).
4. McCarthy, J. A., *Sewage Works J.*, **21**, 75-83 (1949).
5. McCarthy, J. A., *Sewage and Ind. Wastes*, **22**, 77-86 (1950).
6. Report Water Pollution Research Board 1939-1945 His Majesty's Stationary Office (1947).
7. River Pollution Commission 1865, 3rd Report
8. Roetman, E. T., *Water Works and Sewerage*, **91**, 265 and 295 (1944)
9. Singleton, M. T., *Sewage Works J.*, **21**, 286-293 (1949).
10. Southgate, B. A., His Majesty's Stationary Office (1948).
11. Symposium, "New Textile Fibers, Fabrics and Finishes," *Ind. Eng. Chem.*, **32**, 1513 (1940).
12. "Textile Fibers," Mathews, 5th Ed.
13. "Textile Wastes," A Review 1936-1950, New England Interstate Water Pollution Control Comm. (1950).
14. Waste Guide, Interstate Comm. for the Potomac River Basin, Wash., D.C. (1947).
15. Water Pollution Research, Tech. Paper 10, His Majesty's Stationary Office (1948).

10. Pulp, Paper and Paperboard

Harry W. Gehm

National Council for Stream Improvement of the Pulp, Paper and Paperboard Industries, New York, N.Y.

The processes and products of the pulp, paper and paperboard industries, as well as the raw materials employed, are widely diversified. Since there are several books^{32,43,34} describing them in detail no attempt will be made to do so in this chapter. Excellent reviews of the literature^{4,8,10,31} pertaining to treatment of pulp and papermill wastes are published annually and for this reason, no extensive bibliography is included herein.

In general, the wastes produced by the industry are of the group classed as organic wastes. These fall in two general classes in regard to their physical state, namely, suspended and dissolved. Rather than deal with these on this basis, since many processes produce both, the material will be presented on the process basis, covering the more important ones producing liquid wastes.

WOOD PREPARATION

Wood not received at mills in the peeled state is barked mechanically or hydraulically prior to being reduced to chips for cooking. When mechanically debarked it is washed with water sprays. Waters discharged from the washing and debarking operations contain bark, wood slivers and a small quantity of dissolved solids contributed by sap. Generally, the bulk of the bark is screened, pressed free of entrained water and burned. The residual effluent then contains only bark and wood fines together with the dissolved solids.

Data from several typical operations show that from 30 to 50 pounds of suspended matter is discharged per ton of pulp produced by this operation, which requires from 200 to 1,000 gallons per ton of product. The oxygen demand (5-day) of these effluents amounts to between 5 and 20 pounds per ton of product, depending upon the season in which the wood was cut and the period of storage.

Effluents from other wood preparation processes, such as the pressing of rejects prior to burning, produce similar sewer losses.

The concentration of suspended matter and BOD in these effluents

varies considerably depending upon the quantity of water used and whether or not recirculation is practiced. In general, they are dilute wastes. A typical analysis follows:

	(ppm)
Total Solids	1,160
Susp. Solids	600
Ash	60
Dissolved Solids	560
Ash	240
BOD (5-day)	250

In mills barking by dry mechanical methods the quantity of waste water from the process consists only of a small amount of log wash water, the contribution of which to the over-all mill effluent is small. In general, wood preparation does not produce a sufficient pollutional load to make it a significant portion of the mill effluent. Hence, this waste is seldom treated by more than screening and then handled as part of the total mill waste.

KRAFT OR SULFATE MILL WASTES

Inherent to every modern kraft-pulp mill is a very efficient waste treatment system since recoveries of over 95 per cent of the chemicals and wood substance in the spent cooking liquor is common practice. The residues such as bark, rejects and knots can be burned or recovered and fiber loss held to a very low level. Hence, the water carried wastes produced are, under normal operating conditions, very dilute and relatively small in gravimetric quantity on the unit basis. Because of the large size of most kraft operations and the correspondingly large water requirement, the effluent from such mills is voluminous and of about the same strength in terms of oxygen demand and suspended solids as sanitary sewage.

With these factors in mind, it appears obvious that under some conditions stream pollution problems could arise despite the high degree of waste reduction brought about by normal mill recovery and disposal facilities. This is particularly the case when the southern location of the bulk of the kraft industry is considered. In the south some streams are often subject to wide variations in run-off, sluggish in velocity and high in temperature. Others are controlled in discharge to a high degree by power dams with too little regard to other uses.

The major objections to the discharge of kraft-mill effluents in respect to the condition of receiving streams when dilution is low are as follows:

Oxygen depletion	Potential toxicity to fish
Unightly floating matter	Color
Deposits of suspended matter	Odor

The importance and seriousness of these vary greatly depending on location, characteristics and usage of receiving streams, as well as mill design and operation. Oxygen depletion is the most common difficulty because of the relatively high oxygen demand load discharged by kraft mills. Toxicity is an important factor because of the presence of substances in the kraft process, which in sufficiently high concentration in a stream can kill fish and microorganisms upon which young fish feed, despite the fact that these are not present normally in kraft effluents in more than minute traces. Color is seldom a problem since most streams receiving kraft mill waste are either naturally colored, and turbid or dilution is sufficiently high so that the added color does not alter the normal color appreciably. Odor and taste problems have arisen in respect to streams receiving kraft effluents. However, this is a rare problem since few mills discharge into waters ultimately used for potable or bathing purposes. It has been reported that fish removed from waters containing kraft effluent have a distinct taste associated with the odor of the mill. Careful tests conducted in Wisconsin under severe conditions failed to yield any evidence that taste could be imparted to the flesh of fish. Problems arising from floating material on surface waters and deposits of suspended matter on the bottom of water courses are fast disappearing due to the general application of better methods and equipment for fiber retention and for preventing bark, rejects and other debris associated with pulping operations from reaching the sewer.

The individual wastes discharged from a modern unbleached kraft mill and their sources are listed as follows:

- | | |
|---|---|
| <p>(1) Wood preparation</p> <p>Wash Water</p> <p>Rejects dewatering effluent</p> <p>Floor drainings</p> | <p>Washout tail water</p> <p>Liquor storage overflows</p> |
| <p>(2) Caustic plant</p> <p>Dregs</p> <p>Slaker grit drainings</p> <p>Overflows</p> <p>Cooling waters</p> <p>Floor drainings</p> | <p>(4) Pulp mill</p> <p>Blowdown condensate</p> <p>Relief condensate</p> <p>Cooling water</p> <p>Turpentine decanter water</p> <p>Tall oil processing waters</p> <p>Floor drainings</p> <p>Overflows</p> <p>Pulp wash</p> |
| <p>(3) Evaporator house</p> <p>Barometric or Surface Con-
denser effluent</p> <p>Jet condensers</p> <p>Cooling water</p> <p>Floor drainings</p> | <p>(5) Wet room</p> <p>Pulp wash and decker seal pit
water</p> <p>Cooling waters</p> <p>Overflows</p> <p>Floor drainings</p> |

(6) Machine room

Machine water overflows
 Saveall filtrates
 Size tank washout
 Cooling waters
 Overflows
 Floor drainings

(7) Power plant and water treatment

Ash sluicing drainage
 Cooling water
 Boiler blowdown
 Softener wash waters
 Sedimentation tank blowdown
 Filter wash water

Considerable segregation of wastes and recirculation of water are generally practiced as examination of the flow sheet accompanying this section will reveal. From 15,000 to 40,000 gallons of water per ton of product are discharged in the manufacture of unbleached kraft pulp and paper or board. The effluent volume depends to a large extent on the type of product, degree of recirculation and the condenser water system employed. The use of surface condensers in conjunction with cooling towers reduces effluent volume appreciably. Such discharges as dregs from the liquor system and grit from the lime slakers are segregated and discharged to lagoons since these residues drain and dry readily.

The BOD discharged from a modern unbleached kraft mill amounts to approximately 50 pounds per ton of product. Suspended solids sewerage generally amount to less than 0.5 per cent of production or under 10 pounds per ton of production. Improvements in recovery systems have, during recent years, reduced the oxygen demand discharged and it appears that in the future the BOD discharged per ton will reach values as low as 30 pounds per ton. Analyses of 24-hour composite samples of the combined effluent of modern unbleached kraft mills are presented in Table 1.

TABLE 1

	Maximum	Minimum	Average
pH	9.5	7.6	8.2
Total alkalinity (ppm)	300	100	175
Phenol. alk. (ppm)	50	0	0
Total solids (ppm)	2,000	800	1,200
Volatile (%)	75	50	65
Total susp. solids (ppm)	300	75	150
Volatile (%)	90	80	85
BOD (5-day) ppm	350	100	175
Color	500	100	250

While these figures may now be exceeded by some older mills, the present tendency toward improving pulp washing and recovery systems in such plants will soon bring them within these limits in respect to effluent concentration.

Van Horn, Anderson and Katz⁴¹ determined that the substances present

in kraft pulp mill waste that are potentially toxic to fish were caustic soda and soda ash, resin acids, mercaptans and sulfides. The soda compounds are not an important consideration since they are not highly toxic and are rarely found in appreciable concentrations in the effluent itself let alone after dilution with receiving waters. The latter three warrant more consideration, for although they are found in only traces in the mill discharge they are toxic in low concentrations as indicated by the threshold values in Table 2.

TABLE 2

	Minnows	Dafnia	May-fly Larvae	Chironomus Larvae
Resin acids	1.0	3.0		50
Methyl mercaptan	0.5	1.0	1.0	50
Sodium sulfides	3.0	10.0	1.0	1,000

Data on the effluent concentrations found for 5 mills of the older type by Van Horn³⁹ indicated that these values were often lower than the threshold value and that at no time were these levels reached in the receiving waters. Since sulfide and mercaptans are readily destroyed on contact with the dissolved oxygen present in receiving waters they are seldom detectable except at the point of discharge. Allen¹ gives analyses of the effluent of a new kraft mill covering concentrations of the most toxic components (Table 3).

TABLE 3

	Average	Maximum	Minimum
Sulfides	0.07	0.5	0.07
Mercaptans	4.29	5.8	3.4
Resin Acids	4.66	18.0	1.6

It can be concluded from this and similar studies that when the dilution ratio of mill waste to receiving stream is 1 to 20 or greater, toxic conditions will not be approached.

While major improvements in the discharge have come and are continuing to appear through processing and recovery plant improvements, some southern mills have found it necessary to treat kraft effluents because of seasonal low flows in receiving streams. The common methods which have been applied are as follows:

- (1) Storage lagoons receiving the entire waste for a portion of the year.
- (2) Storage lagoons receiving segregated stronger wastes.
- (3) Oxidation lagoons retaining the waste for a sufficient period to allow considerable purification to take place.

The first of these methods is limited to locations where extremely large natural storage facilities can be provided without requiring tremendous construction work. Where such a procedure is possible, it is very effective since all waste is retained at low run-off and discharge can be regulated at high flows in such a manner that the concentration of the waste never reaches a point where the natural purification capacity of the receiving stream is taxed. It has been employed by southern mills located on streams practically devoid of flow during substantial portions of the year.

The second, or waste segregation system, is generally employed where the receiving stream is capable of handling the normal discharge but would be subject to overload by stronger surges. This system employs a small lagoon to which floor drains, overflows and other potential sources of strong waste are connected, hence preventing their entrance to the outfall sewer. Generally, an equalization tank is provided in the common sewer, agitated by aeration, in order to even out the strength of the normal flow. During periods of higher stream flow, contents of the lagoon are pumped at variable rates to the influent of the equalizing tank, the rate being determined by the strength of the lagoon contents and the flow in the stream.

The third, or oxidation lagoon system, is described by Porter, Carpenter and Gehm,³⁰ Porter and Bishop,²⁹ and Crawford.⁹ Results obtained in actual installations are presented in the articles. After removal of the settleable suspended matter, the waste is stored for a period of about 20 days. During this time microbial oxidation occurs and the BOD of the waste is reduced from 60 per cent in the case of kraft waste alone to as high as 80 per cent for combined bleached kraft and groundwood waste. Color is not reduced to a substantial degree.

Moggio,²¹ Moggio and Gehm^{20,22} and Barnes, Moggio and Colner² present laboratory studies on the mechanism of this process, means for stimulating it, and the nature of the bacteria responsible for it. From these studies it appears that a short period of preaeration in the presence of a seed sludge and the addition of nutrients in the form of nitrogen and phosphorus salts could reduce materially the storage period required for oxidation.

Efforts to develop methods for treating this waste with chemicals are described by Moggio.²³ The most promising found to date is coagulation with high calcium lime followed by recarbonation. Removal of most of the color and from 30 to 60 per cent of the BOD can be obtained by this treatment. However, lime dosages required were high and the sludge produced voluminous and resistant to dewatering. Research on this process is currently directed toward developing methods for producing a

dewaterable sludge which could be incorporated in the lime recovery system of the mill.

Research on the odor of kraft waste and its reduction was conducted by Van Horn.⁴⁰ Chlorination was found to provide some reduction in odor and taste. The same author³⁸ also reported on the use of pH as an index of pollutorial strength of the waste. This value, like conductivity which is widely used in practice, was found to correlate well with the dissolved solids and BOD content of mill discharge.

Soda Mill Wastes

The soda pulping process in modern practice is very similar to the kraft in respect to operation and recovery. The only essential difference is that either caustic soda alone or a lower concentration of sodium sulfide than that employed for kraft is used for cooking the wood. Hence, the effluents produced by kraft and soda are very similar in strength and character with the exception that those produced from soda cooks have a considerably lower sulfur content.

SULFITE PULPING

The major pollution problem of the pulping industry is calcium base sulfite waste liquor. This waste contains the residues cooked from the wood by a solution of calcium bisulfite and contains in addition to the spent chemicals between 40 and 55 per cent of the total wood substance. Since recovery is not an integral part of the process, disposal or utilization of this residue must be made. Over three million tons of waste liquor solids are produced by sulfite pulp mills in the United States annually. About 10 per cent of this quantity goes into by-products or is burned, the remainder being discharged into surface waters. Fortunately a large percentage is discharged into tidal waters which provide rapid dilution.

TABLE 4

	% of Total
Sulfur dioxide	11
Sugars	63
Fatty acids	12
Alcohols, furfural, etc.	13

The major constituents of sulfite waste liquor are pentose and hexose sugars and calcium ligno sulfonate, the former being responsible for the major portion of the BOD, and the latter color. Other constituents responsible for oxygen demand are free sulfur dioxide, fatty acids, acetone, methanol, fats, furfural cymene, and other cellulosis residues. Tyler, Maske and Breuer³⁷ present Table 4 in reference to 5-day BOD.

The quantitative analysis of liquors varies considerably depending upon

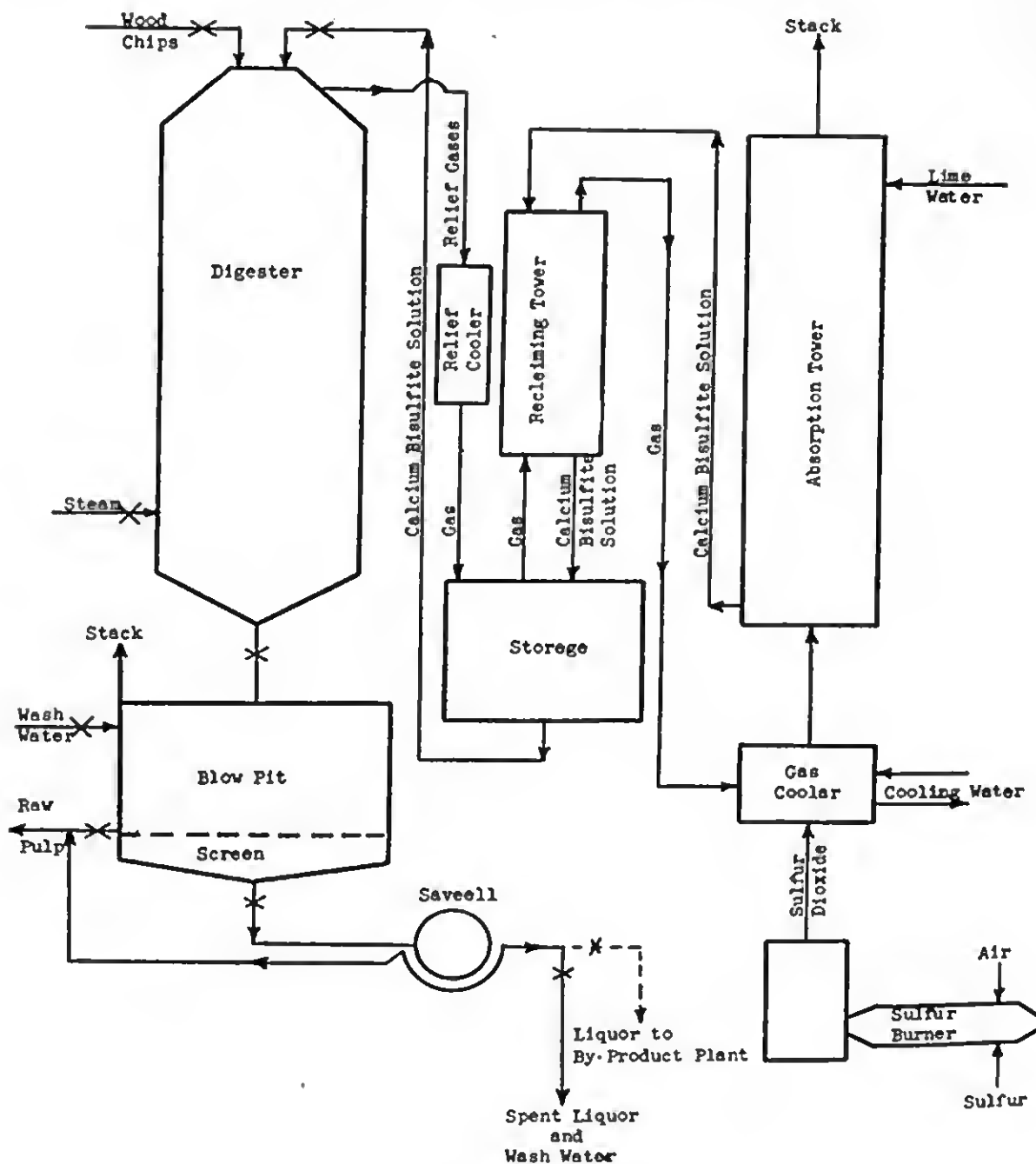


FIGURE 2. Sulfite pulp process

the species of wood pulped, the season in which it was cut, the period of storage and the cooking technique. A general analysis of a typical sample as reported by Klason¹⁶ follows: The constituents are in pounds per day tons of fiber produced.

Lignins	1,198
Sugars	651
Calcium oxide	179
Sulfur	400
Resins fats, etc.	57

The oxygen demand of the liquor varies with the composition. This is particularly true of the sugar content since this accounts for from 60 to 70 per cent of the 5-day BOD. Between 550 and 750 pounds of BOD are discharged per ton of pulp produced. About 50 per cent of this is in the form of concentrated liquor (10 to 12 per cent solids) and the remainder diluted to progressively lower concentrations with wash water, the concentrated liquor ranging from 35,000 to 50,000 ppm in 5-day BOD.

A review of all literature prior to 1940 and an examination of over 800 patents³ pertinent to utilization of waste sulfite liquor resulted in conclusions stated at that time to the effect that "there is no present method of treating waste sulfite liquor that has been shown to be universally applicable from an economic standpoint." As of this date, there appears to be no reason to alter the earlier conclusion. Although there are several processes which, under specialized and favorable conditions or in limited output, have been found practicable for the utilization or treatment of waste liquor, the extension of such processes outside of the favorable circumstances cannot be expected. However, effort continues in the direction of corrective measures.

Sewage Treatment Methods

Comprehensive experimentation upon both large and small scale has been conducted by both educational institutions and industry in an attempt to apply and adapt microbial oxidation processes, such as used to treat domestic sewage, for sulfite liquor.

Activated Sludge. Tests of the activated sludge process conducted at the University of Wisconsin and by a large sulfite pulp manufacturer in the Northwest—both indicated that the process was entirely unworkable except for the treatment of a very small amount of waste liquor in a large volume of sanitary sewage. Foaming difficulties were encountered under even ideal conditions of dilution.

Trickling Filter. Trickling filter tests conducted by Tyler³⁵ and by Holderby and Wiley^{13,14,25} demonstrated the impracticability of the treatment process. Large scale pilot plant tests at a Wisconsin mill over a period of three years demonstrated that 60 per cent of the BOD of the waste liquor could be removed at loadings of 4 pounds of BOD per cubic yard of stone (6453.2 lbs BOD per acre foot). The effluent which was produced had a poor appearance due to masses of microorganisms dispersed in the waste despite secondary settling, and the final color was much darker than the influent. In order that the process work, great pre-dilution was necessary, large stone was required (reducing surface area per unit volume of stone), forced ventilation was required, and nutrients in the form of ammonia and phosphates had to be added. In addition, efficient operation necessitated preheating in cold weather. Corrosion-

resistant or acid-proof construction materials were required. It was found necessary to dispose of large quantities of slime, consisting mainly of wild yeasts and molds, which settled from the waste after passing the filter. Calculations based upon the data of these tests indicated that a trickling filter plant capable of treating waste liquor from a 200 ton mill would be comparable in both size and cost to the mill itself. Operating costs alone would impose a prohibitive penalty upon production costs, and continuous operation of the process would be difficult.

Foam Phase Aeration. Aeration of waste sulfite liquor has long been proposed as an alleviation measure. A modified treatment process was evolved by Logan and Heukelekian¹⁹ wherein the natural tendency of the liquor to foam was employed to accelerate the oxidation. BOD reductions as high as 70 per cent were obtained in the laboratory. The process was not carried to the development stage because of obviously high fixed costs involved in foam treatment structures capable of retaining ten times the daily liquor volume for 12 to 24 hour retention times, and in the provision of an air requirement of approximately 500,000 cfm. Operating costs were considered to be high. If the system were developed, it could not be built and operated at costs substantially lower than a trickling filter installation, and it is doubtful that the foam aeration would be a more practical treatment method.

It is pertinent to mention that the same conclusions have been expressed with regard to other sugar bearing wastes with similar foaming properties.

Fermentation Processes

Two fermentation processes are in use today in sulfite mills in this country. One mill produces *Torula* yeast for stock feed, and the other ethyl alcohol. Both processes are capable of reducing the BOD of waste liquor from 40 to 60 per cent and both have advantage over purely alleviation processes of the recovery of a marketable by-product.

Fodder Yeast Production. The production of fodder yeast from sulfite liquor appears to hold promise as a means of BOD reduction and with provision of some return to cover, to some degree, the cost of operation. The size of the feed market provides an attractive possibility for handling large quantities of liquor. Yeast production processes have been operated in Sweden and Germany, and since protein feeds command a relatively high price in the Northwest United States, possibilities of production in the latter area appeared attractive.

Oregon State College has evaluated the possibilities of fodder yeast production.²⁰ Results indicated an over-all BOD reduction of 40 per cent could be expected; however, the production cost was such that operations could not be insured under normal market conditions in competition with

competitive feed substances. The accuracy of the finding is evidenced by the fact that two of the three Swedish plants which produced fodder yeast have closed recently due to competition. If such a condition prevails in Europe, it would most certainly be expected in this country for large-scale operation.

Because of possibilities of a reduction in operating costs by production of protein feed from filamentous molds rather than yeasts, further investigations were sponsored by the industry in this connection. Although lower operating costs could be achieved, the feeds produced were of lower protein content than the fodder yeast, hence the final economics of mold production were little different than for yeast production.

A large-scale plant built at a Wisconsin mill for the manufacture of fodder yeast has made progress in establishing markets and is currently in operation. The company has most recently announced a consolidation of effort by stock purchase from ten associated mills in order that the fodder yeast development be brought under single company management. The purchase agreement provides for distribution of technical information through the Sulphite Pulp Manufacturers' Research League.

Alcohol. Only one mill in the country manufactures ethyl alcohol from sulfite waste liquor. This process reduces the BOD of the liquor by conversion of the simple sugars and has a designed capacity of 6,140 gallons per day of 190 proof product.

Because of large price differentials in normal times between alcohol from molasses, from ethylene, and from other fermentation processes, production from waste liquor is not attractive in this country. The mill now producing operates by virtue of the fact that the plant was obtained as a war asset item at a low capital cost and is situated strategically as regards markets.

Evaporation

Evaporation, or evaporation and burning, has long been proposed and intensively studied in connection with sulfite liquor. Due to low solid content of the liquor and the corresponding large amount of liquid to be evaporated, heat requirements are high and costly, and corrosion-resistant equipment is required. Evaporation without recovery of a by-product appears to be uneconomical and results in a large volume of residue which is, in some degree, comparable in pollution rating to the original liquor.

Evaporation for the purposes of producing a marketable commodity has been completely investigated. A number of limited markets such as linoleum cement, core binder, ceramic hardener, and as a constituent of insecticides and fungicides has been developed, but such market would not account for more than 5 per cent of the liquor produced. At present,

about 5 mills are capable of supplying the entire demand for concentrated products from evaporative processes, and the entry of more mills into the limited market would destroy it altogether.

Stream Aeration

An ameliorating method for improving conditions in a stream polluted by sulfite liquor was investigated on the Flambeau River in Wisconsin. This method consisted of adding dissolved oxygen to the stream at the point where oxygen depletion is greatest, by means of compressed air diffusion. This serves to accelerate self-purification of the stream and shorten the distance of passage required for oxidation of the waste. Actually in this instance an upper uninhabited stretch of the river was employed for waste treatment for the purpose of insuring improved conditions in the lower inhabited area. Considerable information was obtained relative to the technique involved by Tyler and the National Council for Stream Improvement,^{26,37} and it is felt that under certain conditions this process showed some promise.

With the anticipated future availability of low cost oxygen an adaption of this process might be developed which would extend its application.

Lagooning

Lagoons have been employed both with and without success for the retention of sulfite waste liquors during low water periods for subsequent discharge at flood flows. Sealing the lagoons against seepage determines the success of storage practice since the liquor exerts a shrinking action on many soils. Most of the common sealing methods have proved inadequate, and the soil becomes pervious to the liquor. Employment of the expedient of lagooning necessitates a large block of land adjacent to the mill site and isolated from any populated area. Objectionable odors must be prevented as well as intrusion of seepage into ground water.

A number of mills are currently conducting experiments with lagoons to develop sealing methods and area control.

The Howard Process

This process consists of a multiple lime coagulation system whereby some chemical is recovered, liquor precipitated, and other residues separated. When first devised, it was believed to be capable of high BOD removals, but with the evolution of better testing methods it was found that reduction was about half of that expected since the wood sugars were not precipitated. One mill in this country operates a full-scale installation, the economy of which is based on the sale of several highly specialized by-products of very limited volume but relatively high value

produced from the precipitated liquor such as vanillin. This one mill has been unable to find large enough markets to dispose of the quantity of liquor precipitate produced despite exhaustive efforts to do so, and a considerable portion must be disposed of by incineration.

Heat Hydrolysis Treatment

Research at Oregon State College has indicated that reasonably high BOD reductions can be attained by heating sulfite liquor to a high temperature under corresponding pressures. Sugars are hydrolyzed to carbon dioxide and water and liquaceous material precipitated in filterable form. Batch processing presented no great difficulty, but continuous operation involved reaction kinetics in order to determine retention times and degree of completion of reaction. At present, a laboratory pilot plant is being constructed to determine feasibility of continuous operation and the possibility of elimination of certain difficulties which were apparent from the laboratory studies. It is hoped that a satisfactory treatment process, economical to build and operate, will evolve from this work, since it has been determined that prolonged times of retention are not necessary and size of equipment may be correspondingly reduced.

Evaporation and Burning

Many attempts have been made to evaporate sulfite liquor to a solid content capable of supporting combustion and subsequently burning. Such attempts have, in general, been unsuccessful due to the usual scaling difficulties in evaporators, corrosion of equipment, formation of fly ash, and the low heat value of the concentrated liquor. It is possible to overcome some of the difficulties, but fundamentally the low solids content of the liquor due to low solubility of calcium bisulfite results in high evaporation costs. The recovered heat cannot compensate for high capital and operating cost of plant.

Base Changes

Currently, much interest is evident in this country in the possibility of substituting such bases as ammonia, magnesia, and soda for calcium. These more soluble bases produce a more concentrated liquor and one more readily evaporated and burned. Magnesia and soda have the added advantage of chemical recovery of the base. Such recovery is extremely important because of the higher initial cost of these bases as compared to calcium. Low ammonia prices prior to the current emergency and lower capital cost for an ammonia base installation have dictated the interest in the ammonia bisulfite process.

All three of these bases (ammonia, magnesia, and soda) are under mill

scale investigation at the present time. Difficulties experienced in all three instances, the initial cost of plant, and the fact that the processes are applicable to only large mills have delayed decisive evaluation upon which extension of the processes can be based. The substitution processes, however, appear to hold the most practical approach for waste elimination by larger mills if and when the processes can be made satisfactorily operative.

Conclusions

There is not as yet any universally simple and economic means of sulfite waste liquor disposal. Even the known methods of alleviation or amelioration are not without attendant difficulties. Some progress has been and is being made toward a solution to the waste liquor problem, and efforts will undoubtedly be continued as demanded by public sentiment and as dictated by conservation practice. Differences in mill size, plant location, and operating conditions will always be such that, when viewed from the standpoint of present knowledge, no single process will serve all circumstances. Accordingly, it remains to continue the exploration of all avenues which may provide a possible answer to the problem.

PAPER MACHINE OVERFLOW WATERS

Paper machine overflow waters fall mainly into four classes. These machine overflows are produced from:

- (1) Processing new pulp into paper products.
- (2) Processing of old papers into board products.
- (3) Processing of pulp combined with fillers into paper products.
- (4) Processing of partially washed new pulp produced on location to board products.

[TABLE 5

	/ Susp. Solids per Ton	BOD (5-day) per Ton
Kraft paper	5	5
Glassine	15	5
Tissue (sulfite)	40	10
Tissue (sulfite and groundwood)	60	15

Stream pollution problems arising from the first type of operation result from the discharge of suspended fiber only. Tissues, glassine, wrapping papers and some specialties fall in this classification. The content of dissolved organic matter is very low, hence, the discharge has little oxygen demand other than that of the fiber itself. Examples of the losses from mills of this type are given in Table 5.

The mills in this list recirculate to a practical degree and are equipped with screen-type savealls. High degrees of recirculation are feasible with some waters of this type, since the low dissolved organic matter content allows high effectiveness of slime control germicides. With others, such as insulating papers, this is not possible since electrolyte content must be kept low. Overflow water from these processes varies from 10,000 to 35,000 gallons of water per ton depending upon the grade of paper manufactured.

While fiber loss is not high, it is generally very fine in character. This makes retention difficult and separation from the machine water overflow requires the use of high efficiency clarification equipment. The major objection in respect to the discharge of these types of machine water occurs in cases of low dilution where the receiving water is rendered turbid. Stream deposits seldom result from this waste because it is so finely dispersed; it does not settle at reasonable stream velocities, is incapable of compaction even when settled, and is rapidly oxidized in receiving waters.

Savings obtained from the recovery of this fiber seldom justify the installation of the equipment required, the cost of its operation, and accessory costs such as for added slime control measures which arise in respect to its reuse. Thus clarification of such machine waters can be looked upon as a waste treatment measure.

Flotation savealls are most commonly used for clarifying machine waters of this type to a high degree. The advantage of such devices is that the fiber is collected in a relatively high concentration and is returned to the system with sufficient rapidity that decomposition or sliming does not occur to a disastrous degree. These are capable, if capacity is adequate, installation proper and control good, of doing a satisfactory job. The major limitation of all such devices are their sensitivity, although this can be greatly reduced by careful installation. More recent devices marketed for this purpose are filtration machines employing diatomaceous or pulp filter aids. These have the advantage of providing a barrier through which the waste water must pass and they are not subject to upset. They can thus deliver continuously a water of a quality which can be re-used in part on showers and similar machine appertenances which cannot operate on water containing appreciable suspended matter at any time. However, installation and operation costs of the filters are decidedly higher than for flotation units.

Both flotation and filtration devices have demonstrated their ability to reduce the suspended solids content of machine waters of this type below 50 ppm and the loss below 5 lbs per ton. This figure does not, however, represent total loss by the mill since flow drains and overflows

contribute some additional continuous loss, and intermittent losses occur on changeovers and wash-ups. The level represents the practical optimum degree of clarification obtained by sewage treatment processes. The data presented in Table 6 shows typical results for filtration and flotation systems operating on machine water discharged from various types of production.

TABLE 6

	Filtration lbs per 1,000	Flotation gals of effluent
Kraft paper	0.05	0.08
Glassine	0.05	0.09
Tissue	0.21	0.20

It appears, therefore, that such stream pollution problems as may arise from the discharge of machine waters of this type can generally be remedied by the installation of a suitable clarification system integral with the mill operation. Further external treatment of the discharge could accomplish nothing in view of the efficiencies obtainable and the fact that recovered residues can generally be incorporated in the product.

The second class of machine water is produced from the manufacture of board products from used papers and boards, mainly news, carton and various heterogeneous mixtures. Water discharged from this operation varies in character due to the types of stock employed, the product manufactured and the degree of recirculation of white water within the mill. The volume of effluent per ton of product varies between 5,000 and 20,000 gallons per ton although a few mills have reduced this to as low as 1,000 gallons. Average discharge for a mill employing savealls and recirculating white water to stock preparation and cylinder showers is about 10,000 gallons.

Most stream pollution difficulties arising from this waste result from the discharge of fairly coarse suspended matter composed largely of fiber and other organic debris. A large portion of this will settle at low-stream velocities, causing the usual problems associated with organic bethal deposits. In addition to the settleable suspended solids, this waste contains some dispersed matter, considerable dissolved organic matter arising from sizing and adhesives, products of cellulose hydrolysis, and other impurities carried in the old paper. Analysis of the effluents from a large number of mills employing a degree of recirculation and simple savealls indicates that suspended solids discharged per ton of product varies from 35 to 70 pounds and a BOD (5-day) of 15 to 30 pounds. From 70 to 90 per cent of the suspended matter is settleable without the addition of coagulants. Reasonably low dosages of alum will cause settling

tinuous sludge removal at a slow steady rate in order to prevent decomposition and sliming of the sludge and to allow withdrawal at a high density. A two-hour detention period at maximum flow will yield optimum results.

Thickener type clarifiers operate well both with and without coagulants; although when coagulation is employed care must be taken to operate the collector in a manner which will prevent stagnation of the sludge in the tank and at the same time allow good thickening. This type is generally designed on the basis of a two-hour detention period at maximum rate of flow.

The third, or high rate type of clarifier, is employed to advantage only when the waste is coagulated. Since the waste flow filters through a blanket of sludge suspended in the body of the tank an exceptionally clear effluent can be produced at detention times and overflow rates as low as one-half that of the usual thickener type clarifier. With this added efficiency goes greater sensitivity to fluctuations in temperature, flow, feed strength and chemical dosage. Hence, installation must be carefully made and operation good if the advantages possible with units of this type are to be realized. Early models of these devices had the disadvantage of delivering a low density sludge but this trouble can be largely overcome by including thickening devices integral to them.

While clarification of these machine waters presents no major problem, handling of the sludge obtained is not generally as readily accomplished. With some furnishes and under certain operating conditions it can be returned to the system and completely incorporated in the product; however, in others it can be partially incorporated and in some it must be disposed of completely. The common method of disposal is lagooning in earth embanked basins. These are filled with sludge which is allowed to compact following which supernatant water is siphoned off. The residue is allowed to dry to a degree where it can be handled, at which time it is collected by means of a bulldozer or drag line and hauled to dumping grounds. Appreciable land in undeveloped areas must be available for this method. An excellent summary of dewatering and drying qualities of such residues upon which actual requirements can be based was presented by Vogler and Rudolfs.⁴²

The third class of machine waters referred to are produced by the manufacture of ledger, book and similar papers containing appreciable quantities of filler materials such as clays and calcium carbonate or sulfate. In many of these waters the quantity of suspended filler approaches that of fiber and since they are extremely finely divided rapid separation from the water is not readily accomplished.

Summarized data covering numerous mills indicate that the overflow

water contains from 50 to 120 lbs of suspended solids per 10 of product and 10 to 25 lbs of 5-day BOD. Of the suspended solids between 50 and 70 per cent are volatile.

Until recently, flotation type savealls were used almost exclusively for clarification of machine waters. Alum in conjunction with glue or resin size must be added to obtain optimum clarification. In some cases, fiber has also been added to the feed in order to insure a sufficiently high fiber-to-filler ration to allow adherence of the filler and maintain a balance in the slurry returned to the machine. Sensitivity is the major shortcoming of the flotation systems operating on these waters, since variations in flow, suspended solids, injected air, chemical dosage and fiber-to-filler ratio all effect the degree of clarification obtained. When operating in balance these devices produce effluents containing between 20 and 50 ppm of suspended matter, and they promptly return a relatively dense slurry to the machine system.

TABLE 7

	Susp. Solids (ppm)	BOD (ppm)
Strawboard machine water	940	430
Saveall effluent	480	310
Semi-chemical machine water	745	1,015
Saveall effluent	290	890

Recently attention has been given to the application of high rate upflow clarifiers to these waters. There is little reason to believe that these will prove any more satisfactory than the flotation units. In all probability, results, operating characteristics, installation and operating cost of the two will prove similar.

The fourth class of machine waters are those containing appreciable quantities of dissolved solids in the form of cooking liquor residues. Strawboard and semi-chemical boards are examples of this group. In these processes the pulp is often incompletely washed prior to delivery to the machines. Since the presence of liquor solids serve as food for slime bacteria and inhibit the activity of germicides, recirculation of the machine water to a high degree in the stock system is not practical and fresh water must be employed for the showers. Typical analyses of these white waters are presented in Table 7.

Saveall devices employed in mills of this type are of screen variety and since the fiber reaching them is generally finely divided removal efficiencies are not high. More efficient clarification devices are not practical because of rapid sliming in recovered slurries, the finely divided nature of the recovered residues, and the high and rapidly varying coagulant demand induced by the presence of liquor solids.

Three methods have been employed for removing the bulk of suspended solids from these wastes. The first necessitates a complete change in the manufacturing process wherein the pulp is washed to a high degree on vacuum filters prior to delivery to the machines. The other two are strictly disposal systems, the older of which is the sedimentation lagoon similar to that employed for news and chip mill waters. More recent is the application of lime precipitation in a clarifier of the thickener type. This system has not met with much success because the underflow discharged from the clarifier is highly hydrous and resists further dewatering even on the addition of impractical dosages of conditioning chemicals.

The first method is most desirable but is limited to only a few operations because of high cost and physical limitations. The second method has been successfully applied where suitable land was available and proper attention given to operation. The third has been a practical failure.

In summing up the machine water problems it can be said that:

(1) Very substantial progress has been made by the pulp and paper industry in reducing suspended solids discharged by paper machine operations.

(2) New equipment and processes are constantly being developed which are leading to the discharge of effluents as low in suspended solids content as highly treated municipal sewage effluent.

(3) Recovery of fiber and filler beyond a certain point is not profitable but imposes an actual cost on the over-all manufacturing operation.

(4) Clarification of some machine waters imposes a disposal problem in that residues separated from the water are not suitable for re-use or on re-use they interfere with the manufacturing process or reduce the quality of the product.

(5) In the case of some machine waters, clarification alone is not sufficient to remove all the objectionable characteristics since the color or oxygen demand imparted to receiving waters by dissolved solids present, can under some conditions, result in surface water problems.

(6) In many cases, particularly with high rate units, proper installation and good operation are more important than the type of equipment employed as far as results are concerned.

DEINKING WASTE

The major waste water produced from the deinking of old paper for the recovery of pulp comes from the washing system. This generally consists of deckers operated countercurrently and employing fresh and spent bleaching waters for the operation.

Washer discharge varies from 20,000 to 30,000 gallons per ton of stock

washed. Both the quantity of water employed and the strength and character of the effluent depend upon the grade and quality of the stock handled, the degree and type of treatment given the stock, and the effi-

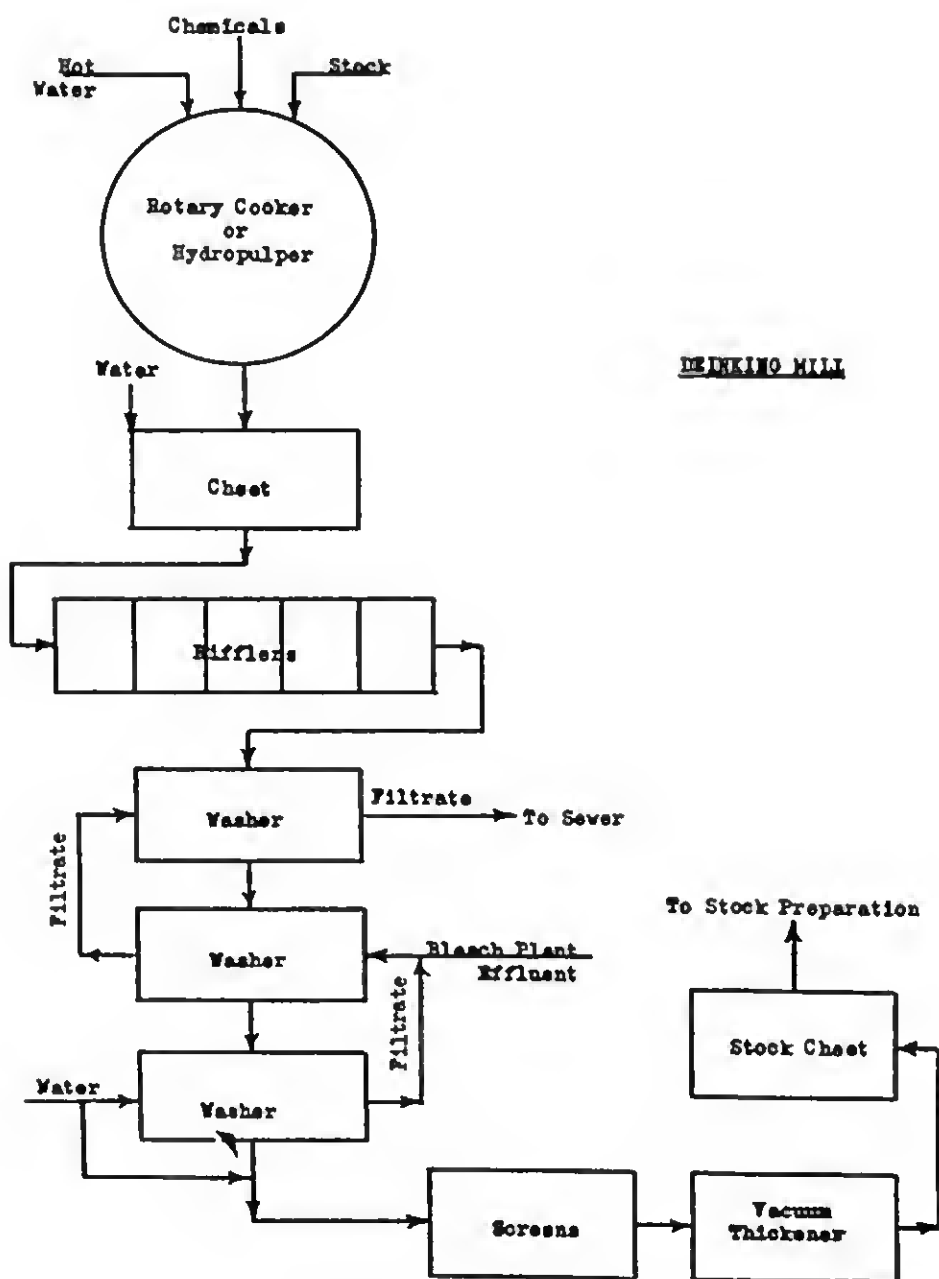


FIGURE 4. Deinking waters

ciency of the equipment employed for washing. For example, papers containing more ink require higher chemical concentrations and more vigorous heating than those low in ink content. Such treatment produces higher

dissolved organic matter concentrations in the washer waste than observed for low-ink content stocks. In addition to ink filling, coating and sizing materials are removed from the pulp to a high degree. This accounts for a shrinkage of from 20 to 40 per cent between the old paper and the washed stock. Hence, the waste contains essentially fillers and fiber debris in suspension together with a considerable quantity of organic matter in solution.

Surveys of 10 mills indicate that from 200 to 600 pounds of suspended solids are discharged per ton of product and from 50 to 250 pounds of 5-day BOD. Average figures amounted to 375 pounds of suspended matter and 120 pounds of BOD.

Swope³³ analyzed numerous samples of waste. Table 8 summarizes the results of these analyses.

TABLE 8

	Maximum	Minimum	Average
pH	12.0	7.4	9.4
Turb. (ppm)	2,500	173	1,220
Alk. Phen. (ppm CaCO ₃)	500	0	131
Total (ppm CaCO ₃)	1,266	123	592
Total Solids (ppm)	5,075	462	2,465
Total Solids (% Ash)	63.0	38.8	53.6
Susp. Solids (ppm)	3,000	46	1,010
Susp. Solids (% Ash)	75.4	21.0	56.3
5-day BOD (ppm)	640	260	440
Total N (ppm)	9.10	2.02	6.24

Sedimentation of deinking washer waste water for a period of 2 hours removes practically all the settleable solids and from 50 to 65 per cent of the total suspended solids. Accompanying BOD reduction varies widely with different wastes, since removals of from 15 to 50 per cent have been observed at plants operating this process. Sludges produced can generally be obtained at consistencies close to 10 per cent solids when mechanical collection mechanisms are operated properly. The sludge dewatered readily on vacuum filters without preconditioning to a consistency of 25 to 35 per cent at rates of from 6 to 10 dry pounds per square foot of filter capacity per hour.

Removals obtained by sedimentation can be enhanced by treatment with magnesium salts or by the elutriating and coagulating action obtained by dilution with paper machine overflow waters containing residual alum. The former method is of limited value because of high chemical requirement. Application of the latter requires about three times the clarifier capacity necessary for handling the waste alone and is difficult

to control because of varying alum content in the machine overflow water. While treatment with magnesium salts does not affect sludge compaction adversely the dilution procedure shows a decided tendency to do so.

A comparison of clarification obtained by the application of magnesium salts as compared to plain sedimentation on washer waste is presented in Table 9.

TABLE 9

	Plain Sedimentation (2 hrs)	Treatment with 1666 to 2075 # M.G. MgSO_4
Reduction in total susp. solids (%)	60 to 65	81 to 96
Reduction in 5-day (%) BOD	20 to 25	34 to 50

Secondary treatment of deinking waste was investigated by Morgan²⁴ in the laboratory and on pilot-plant scale. It was concluded from these studies that the waste could be treated by a biological aeration process and on the basis of this conclusion a large-scale plant has been built in Michigan to determine if this process can be successfully integrated with mill operation. Data will be obtained on efficiency in relation to capital and operating cost. Pilot plant tests indicated that a BOD reduction of about 68 per cent could be obtained with an aeration period of 6 hours if sodium nitrate was added to the waste to increase its nitrogen content.

Sludge

The major problem in treating deinking wastes is disposal of the sludge. Filter cake is produced by primary treatment in about the same tonnage as deinked pulp produced. All attempts to utilize this material have failed mainly because of its variable composition and high moisture content. Because of the high ash content, incineration has been found impractical. Some attempts to lagoon it prior to dewatering have been unsatisfactory due to odors resulting from decomposition. This difficulty has not appeared when dewatered sludge has been disposed of on land. Land fill appears to be the only satisfactory method of disposal and since on freezing and thawing further moisture is lost from the filter cake a soil capable of bearing normal loads is eventually produced. This is particularly the case when rubble soil and other dryer and heavier fill materials are employed with it. The relatively large fill area required for even a small deinking operation limits this method of disposal.

STRAWBOARD WASTE

Three major waste waters are produced from processing straw into paperboard products. These are as follows:

- (1) Blowdown liquor from the digesters in which the straw is cooked.
- (2) Washer-beater water from beaters in which the pulp is washed.
- (3) Machine overflow water.

The first of these is small in volume and is generally mixed with the beater wash effluent. The latter two account for the large bulk of the 25,000 to 35,000 gallons discharged per ton of product, the wash accounting generally for two-thirds of the total.

Stream pollution problems resulting from the discharge of strawboard waste in order of their importance are solids deposition, oxygen depletion and color. The first is by far the most common and the third only important in a few instances.

Bloodgood⁵ gives the following analysis for these wastes in Table 10.

TABLE 10

	Total Solids (ppm)	Vol. (%)	Susp. Solids (ppm)	BOD (5-day)	Total N	Total P ₂ O ₅	Total K ₂ O
Total waste:							
Average	3,835	68	1,707	847	1.18	0.42	0.77
Maximum	4,660	70	2,110	980	2.43	0.87	1.71
Minimum	3,243	64	1,215	525	0.62	0.15	0.14
Machine water:							
Average	2,729	72	931	314			
Maximum	5,036	89	1,520	430			
Minimum	1,278	60	560	198			
Washer beater:							
Average	7,095	69	2,951	1,665			
Maximum	8,925	71	3,240				
Minimum	5,685	68	2,650				

Lardieri¹⁸ gives the following analysis for rotary liquors which accounts for from 15 to 20 per cent of the total solids of the waste.

	(ppm)
Total solids	79,000
Total volatile	61,200
Per cent volatile	77.4
BOD (5-day)	32,000
pH	8.2

The volatile solids consist mainly of cellulose, pentosans and lignins; the ash consisting principally of sodium, salts, calcium oxide and silica.

Since a large portion of the suspended matter present in this waste is in the colloidal state reductions in total suspended solids effected by settling for short periods of time are low, generally running from 40 to 50

per cent. Twenty to 30 per cent of the BOD is removed by settling, and sludges produced average two per cent solids. On long periods of sedimentation agglomeration of the colloidal sols takes place through bacterial activity.

Over 75 per cent of the suspended solids can be removed by coagulation and settling with hydrated lime applied at a rate of 1,500 pounds per million gallons.

Sludges produced by sedimentation and lime coagulation are hydrous and odorous and resist dewatering by the methods commonly employed for this purpose. Partial dewatering has been obtained by Bloodgood⁶ by the use of excessive dosages of iron salts and lime but the amounts of conditioning chemicals necessary rendered the process commercially impractical. Eldridge and Mallmann¹¹ reported strawboard sludge resistant to anaerobic digestion. Some recent results obtained at a sewage treatment plant handling a considerable percentage of the waste indicate that it digests readily in combination with sanitary sewage solids. Observation of deposits of long standing in lagoons receiving this waste indicate that considerable decomposition does occur but little is known concerning the rates of digestion other than the original work of Eldridge and Mallmann. It is possible that the recent methods of straw processing may result in a more rapid decomposing sludge. This matter is currently being investigated by Bloodgood.

Anaerobic treatment of the entire waste was practiced by Kessener¹⁵ in Holland. Long periods of digestion produced effluents of good quality. Digester capacities as employed in this work are impractical from the standpoint of waste treatment; the primary purpose of this system having been gas production in an area where fuel costs were exceedingly high. Bloodgood⁶ studied high rate anaerobic digestion of pre-settled waste in both the laboratory and in a pilot plant designed by Morgan and Gehm¹² especially for treating this waste. Although laboratory experiments indicated that BOD loadings of 0.1 lb/cu ft digester capacity could be obtained at reductions as high as 90 per cent, equivalent results have not been obtained to date for more than short periods of time in the plant.

Trickling filter treatment was also investigated by Bloodgood⁶ on a pilot-plant scale. Reductions in BOD obtained in relation to filter loadings at 80°F are shown in Figure 5.

At lower temperatures filter efficiency dropped sharply and Bloodgood concluded that because of this the trickling filter does not represent a satisfactory method of treatment for strawboard waste.

Krancher¹⁷ describes the operation of lagoons at an Indiana mill. It was found that settling and controlled storage during the summer months

produced an effluent equivalent to that obtained by the trickling filter treatment. The sludge deposited in the settling portion of the basins decomposes anaerobically, will dry to a condition in which it can be handled, and can be utilized as a soil conditioner. In order to prevent odor troubles the capacity must be large since a considerable volume of seed sludge must be maintained in the settling areas to prevent septicity. It has been demonstrated that the presence of sanitary sewage greatly accelerates the rate of purification of the waste on storage.

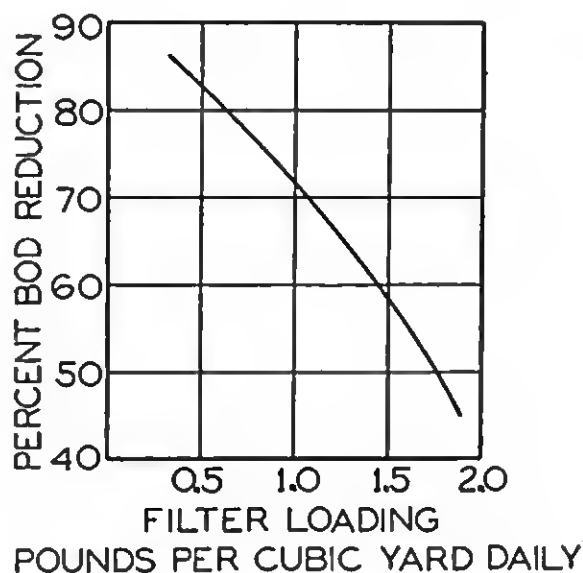


FIGURE 5. Strawboard waste

This method appears to be the only satisfactory means of treating strawboard waste with reasonable economy. There exist, however, possibilities of reducing the pollutional load from these operations by means of processing changes. Straw as received at the mills contains considerable extraneous material which contributes little to the product but much to the waste load. If this could be removed prior to processing, a substantial reduction in BOD and solids content of the waste would result. Attempts to do this have not met with success to date because of the varying moisture content of the straw. Use of a sugar press to remove a large portion of the cooking liquor in a concentrated state prior to washing has been tried. The small volume of strong liquor can be seasonally lagooned in a relatively small impoundment, thus reducing the BOD of the discharge during critical periods. However, this technique does not reduce substantially the suspended solids problem which is the most pressing in many instances. The discovery of a satisfactory method for dewatering and disposing of primary sludge would lead to the greatest over-all stream improvement advance in this branch of the paper industry.

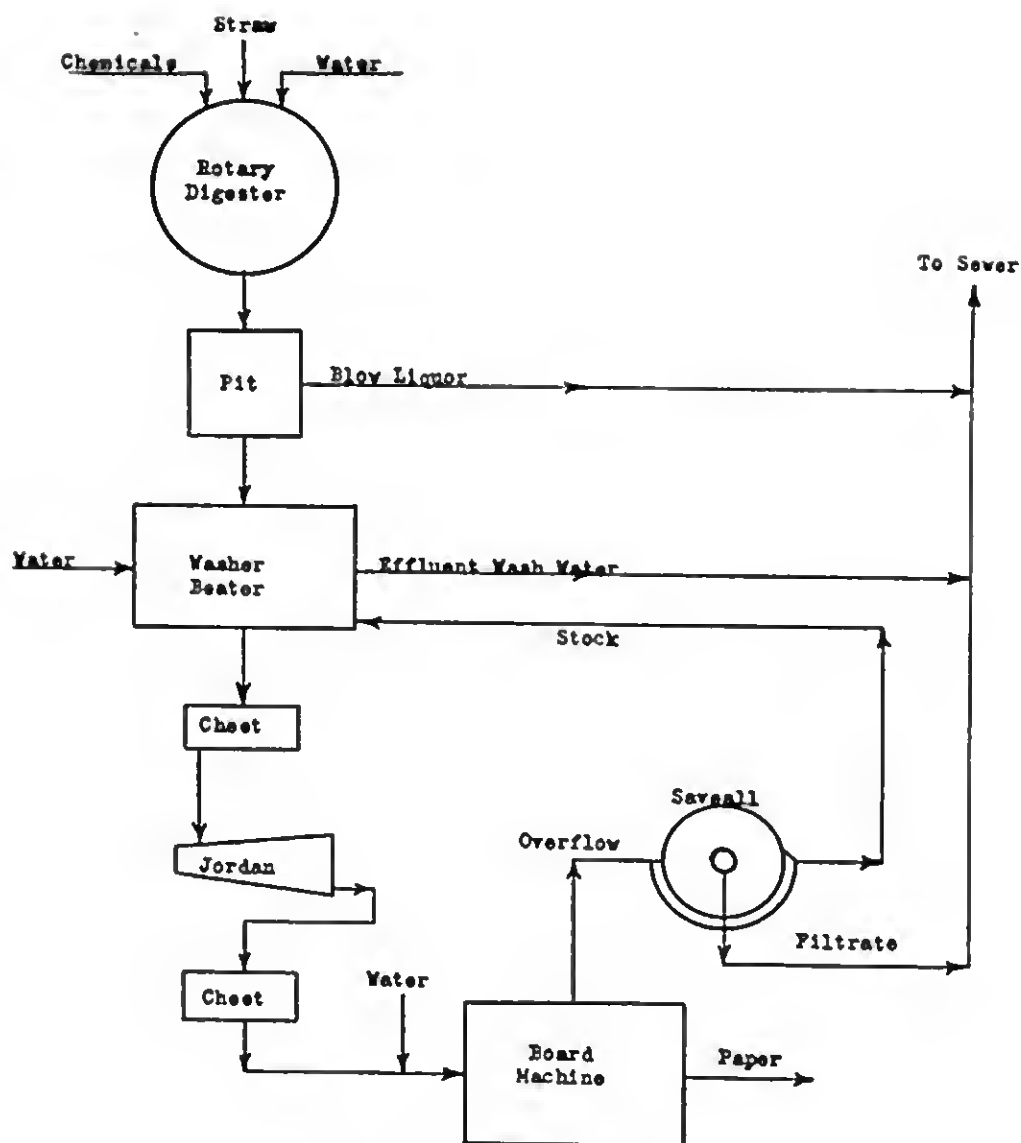


FIGURE 6. Strawboard mill

RAG, ROPE, JUTE AND FLAX PULPING

Pulp produced from rags, old rope and jute products as well as flax straw are manufactured in small operations ranging from 5 to 25 tons daily. In the case of rope, rag and flax, a cooking operation is generally employed, while jute is often pulped directly in beaters to which hot water and chemicals are added. Flow sheets typical of each system are given in this chapter.

A number of wastes are common to these processes. When cooking is practiced a blowdown liquor is obtained on relieving the digesters and in some cases a pre-seouring is used, the liquor from which is discharged

from the digester prior to cooking. In some instances the blow liquor is fortified and re-used for a second cook. Washing is usually done in the beaters, and this operation produces the greatest volume of effluent.

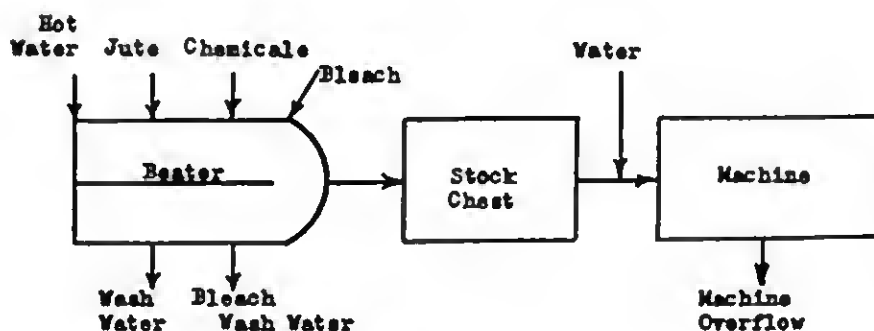
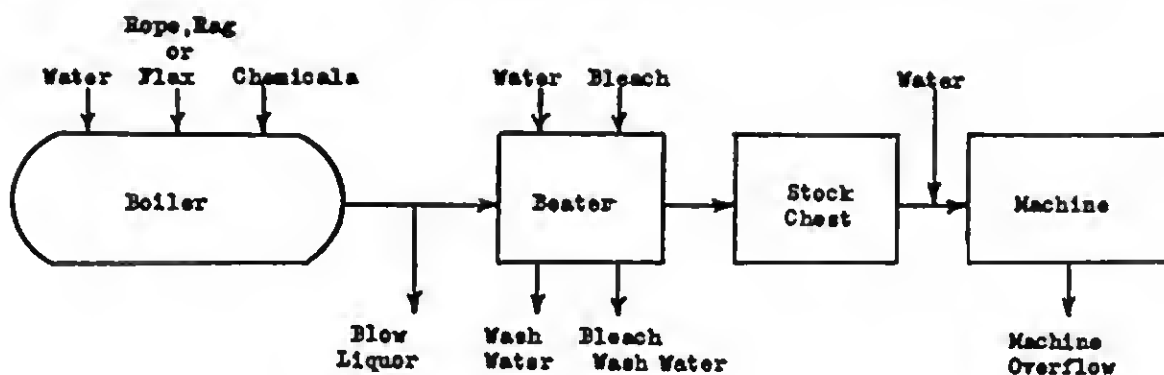


FIGURE 7. Rag, rope, flax and jute pulping

Bleaching, when practiced, is also done in the beaters, as is the washing which follows this operation. The washing produces another waste. Table 11 contains average figures for these operations.

TABLE 11
Quantity Per Ton of Product

	Vol. (thous. gals.)	Total Solids (lbs)	Susp. Solids (lbs)	BOD (5-day) (lbs)
Jute	65	922	281	316
Rope	75	1,360	277	1,213
Rag	80	2,600	474	707

Jute cooking liquor has a BOD of around 3,500 ppm, rope cooking liquor 15,000 ppm, and rag 30,000 ppm. About 2,000 gallons of this liquor are produced per ton of product. The bulk of the cooking liquor washed from the pulp is contained in the first third of the total volume of wash water. Hence, the major portion of the pollutional load from these operations is contained in the combination of the cooking liquor and first washings. Detailed average analysis of these liquors and corresponding composite wash waters are presented in Table 12.

TABLE 12

	Rag		Jute		Rope	
	Blow Liquor	Wash Water	Blow Liquor	Wash Water	Blow Liquor	Wash Water
pH	11.1	8.1	12.0	11.2	12.0	8.0
Total alkalinity	30,500	447	2,850	574	21,000	198
Org. N.	1,190	31	126	6	98	39
Total solids	103,500	2,046	7,187	1,332	39,869	1,105
Volatile (%)	62	61	56	56	48	61
Ash (%)	38	39	44	44	52	36
Susp. solids	8,550	630	1,238	467	311	451
Volatile (%)	87	70	44	67	68	83
Ash (%)	13	30	56	33	32	17
BOD (5-day)	32,500	418	3,380	385	14,862	2,731

Blow-off liquor has been treated by three methods on mill scale—evaporation and dumping the residue, chemical coagulation, and lagooning during low stream flows. If evaporation could be accomplished by tubular evaporators, this means of disposal would be quite attractive. However, foaming difficulties have prevented successful evaporation by any except the costly drum method, hence this means of handling the waste has not achieved ready acceptance.

Chemical coagulation can be produced by heavy dosages of alum and calcium chloride. A mill employing this process on a 20,000 gallon batch basis obtains the following results (Table 13).

TABLE 13

	Untreated (ppm)	Treated (ppm)	Removal (%)
BOD (5-day)	7,900	4,800	38
Total solids	36,650	24,530	33
Color	67,500	20,500	70

Sludge volume 10 to 15% of total.

It will be noted that the most marked reduction obtained is in color, the liquor being reduced from a black to an amber shade. The sludge produced is very resistant to dewatering and is lagooned. Similar results were obtained in the laboratory on treating rag and jute liquors. In general, chemical treatment does not provide a great deal in purification in

relation to its cost together with the fact that it produces a sludge which cannot be drained or filtered.

Lagooning of the cooking liquor seasonally appears to be a useful abatement method because of the small volumes involved, but is limited to uninhabited areas due to the unpleasant odor of the material, particularly when hot.

Both biological and chemical treatment of mixed wastes have been investigated. The latter is decidedly limited in application due to high chemical dosages, low degree of purification obtained, and the voluminous sludges produced. The former appears to be more promising although the waste does not respond as well as others to biological oxidation. Trickling filter experiments indicated that rope mill waste diluted with machine water could be reduced 50 per cent in BOD, if nutrient salts were first added, at loadings of 1.5 lbs of BOD per cu yd of filter capacity per day. Rag mill waste appeared a little more amenable since higher BOD reductions were observed at a similar rate of application. Recent tests with an aeration system operating on combined liquor and first wash water, which was neutralized and supplemented with ammonia and phosphates, have indicated that high BOD reductions could be obtained. However, long aeration periods appeared necessary to produce these results.

SEMI-CHEMICAL PULPING WASTES

Semi-chemical pulps are those produced by modifications of the common chemical pulping processes. In general, a more dilute cooking liquor is employed and the period of treatment shorter than for true chemical pulps. These processes provide larger yields since less wood substance is removed and permit the use of hardwoods. Three processes are in use. These include soda, kraft and neutral sulfite, the latter being the most common.

In a number of cases these processes are operated in conjunction with kraft mills in which case the kraft recovery system absorbs the bulk of the spent cooking liquor solids. Where not integrated with a chemical pulp mill, recovery is not practiced because of the low concentration of the liquor, the extreme corrosiveness of neutral sulfite and the difficulty of recovering the chemical in a useable form. A number of attempts have been made to develop recovery systems but until recently all have failed. A system presently being investigated shows considerable promise but it is unlikely that one can be developed which will be economically advantageous because of the amount of water which must be evaporated from the liquor in relation to the heat value of the liquor solids and the relatively small quantity of recoverable chemicals.

A typical neutral sulfite semi-chemical flow diagram (Figure 8) ac-

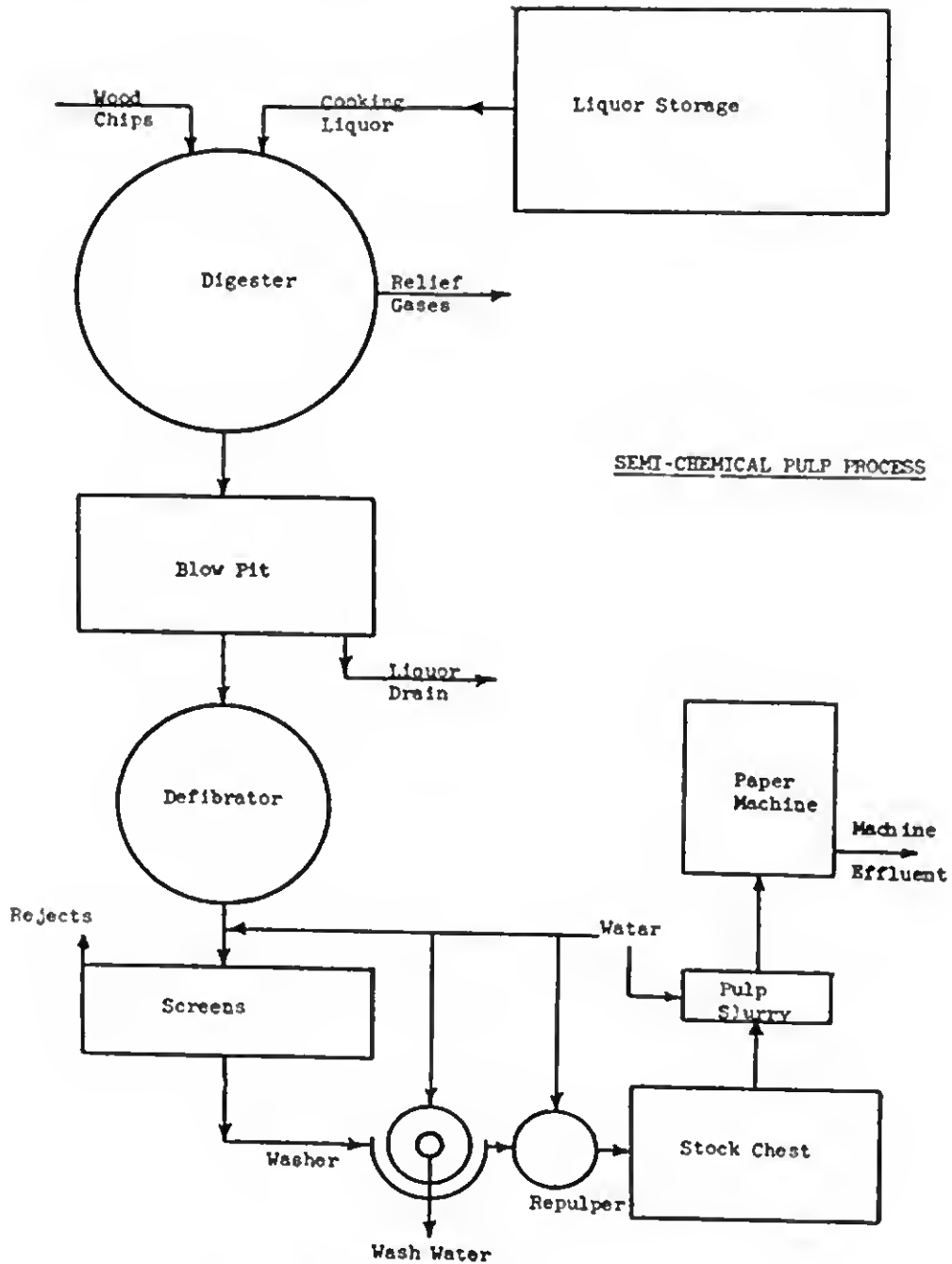


FIGURE 8. Semi-chemical pulp process

companies this section. Three major wastes listed below are generally produced.

- (1) Strong spent liquor blown from digester.
- (2) Weak spent cooking liquor discharged by pulp washer.
- (3) Machine water which generally contains some liquor solids due to the fact that the pulp does not lend itself to thorough liquor removal on washing.

The objectionable features of semi-chemical wastes are their oxygen demand and color. Field investigations have demonstrated them to be non-toxic to aquatic life in stream concentrations sufficient to cause considerable but not complete oxygen depletion. Salts of lower fatty acids (mainly acetates) and pentosans account for most of the oxygen demand; lignins and tannates the color. An appreciable amount of finely divided fiber is generally lost in the process which can give rise to the difficulties associated with suspended matter in surface waters when stream velocities become very low.

Table 14 gives typical values for a mill producing an average of around 120 tons daily²⁸:

TABLE 14

	Digester Blowdown	One Stage Washer Effluent	Machine Effluent
Volume (gal/day)	24,000	2,000,000	864,000
Solids			
Total (ppm)	102,300	4,593	658
Fixed (ppm)	35,000	1,547	166
Volatile (ppm)	67,300	3,046	492
Total (tons per day)	10.8	38.3	2.4
Color (ppm)	165,000	12,000	500
BOD (5-day)	1,940	16,440	230

Holding lagoons from which discharge of the stronger wastes are controlled in accordance to the flow of receiving waters have been employed to handle semi-chemical waste problems. This system is of limited use in warmer climates since aerial nuisance can be caused by decomposition. Because of this the lagoon must be placed reasonably far from inhabited areas.

Seepage of the liquor into sandy soils as a method of disposal is in use in several instances. Work with this method has not progressed far enough to allow definite conclusions to be drawn. At best, however, this means of handling the waste will be limited since its success depends on the existence of suitable soil conditions close to the mill.

The recovery of acetic acid from semi-chemical pulping liquors can

be and is accompanied by a considerable BOD reduction. It is evident from examination of costs that this process is not competitive at present.

Semi-chemical wastes have been treated by lime precipitation in a full scale treatment plant. Removal of the bulk of the color and about 25 per cent of the BOD was achieved. However, because of the voluminous nature of the sludge produced and its gelatinous characteristics, as well as process control difficulties, the process was not adopted by other mills.

Research²⁸ has indicated that when supplemented with nitrogen and phosphorus, the wastes can be oxidized by aerobic methods and can be digested by anaerobic decomposition. While relatively high BOD reduction can be obtained at normal loading rates little color reduction takes place. These processes have not been employed because of the enormous size of the installation required for even a small mill. An idea of this requirement can be obtained from an article by Buswell and Sollo⁷ in which digester requirements are presented for a mill using only a light cook.

It has been established that these wastes can be treated together with sanitary sewage in municipal plants if the volume does not exceed about half the total flow and adequate capacity is provided to handle the total load on a solids and BOD basis.

BLEACHERY WASTES

The major wastes produced by pulp bleaching are those obtained from treating sulfite, kraft and soda pulp. While the processes employed are varied in respect to the number of stages employed, the flow diagram (Figure 9) illustrates the basic process. Two wastes of dissimilar reaction are produced, namely, acid waste from the chlorine and hypochlorite stages and alkaline waste from the caustic extraction stage. The acid wastes are characterized by their low concentration in terms of oxygen-consuming substances and color as well as their high volume. The caustic extract is high in oxygen demand and color but much lower in volume than the acid wastes. Combination of the two generally produces a waste substantially neutral in reaction in a volume of from 30,000 to 60,000 gallons per ton of pulp bleached. The color is due mainly to lignin salts and the oxygen demand to cellulose degradation products.

Analysis of combined bleachery discharge is generally within the range of the following values:

pH	4.5 to 8.0
Turbidity	60 to 300 ppm
Total Solids	1,000 to 2,000 ppm
Volatile	45 to 65%
Susp. Solids	50 to 75 ppm
Volatile	40 to 70%
BOD (5-Day)	50 to 100 ppm

The combined waste can be coagulated with lime. Such treatment will remove most of the color and from 25 to 50 per cent of the BOD. Sludge produced from lime treatment is not dewaterable and this fact has prevented the use of the process. To overcome this shortcoming, experimental work on lime precipitation followed by recarbonation is in progress and if successful may lead to integration of this method of treatment with the lime recovery system of kraft and soda mills. It is believed that a portion of the water so treated can in some cases be re-used in the bleachery, thus reducing the high water requirement.

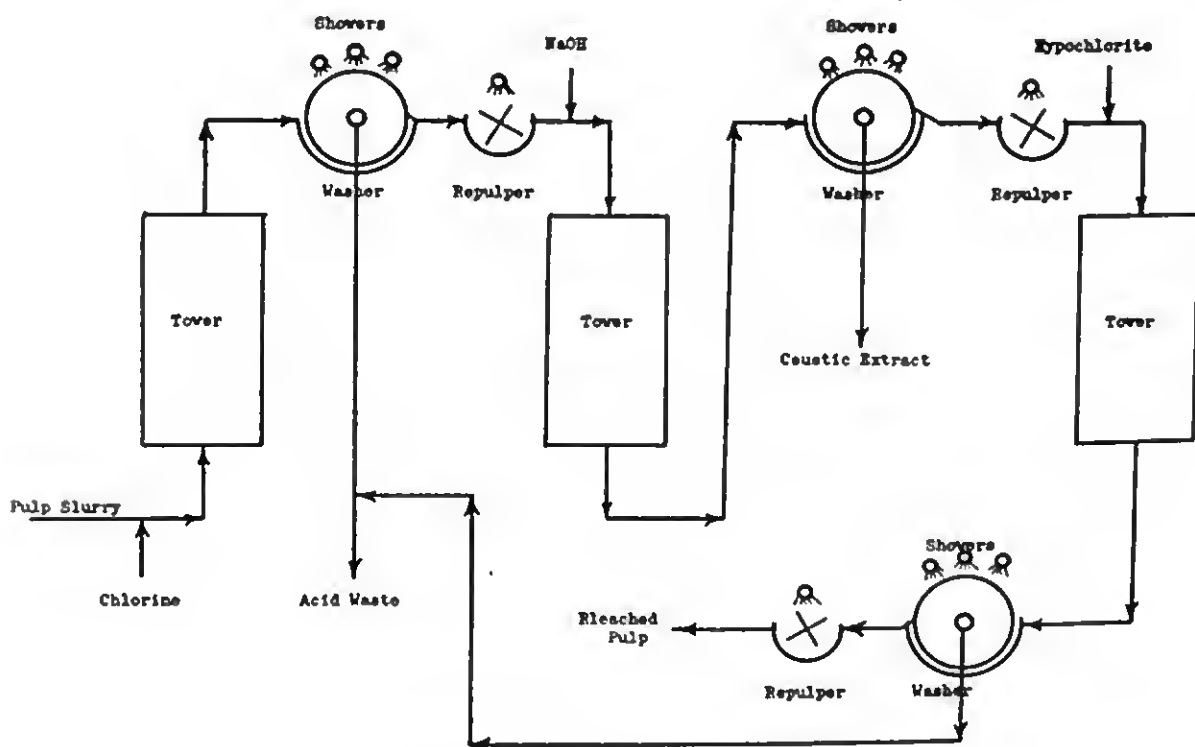


FIGURE 9. Bleaching wastes

The oxygen demand of bleachery effluents is reduced on storage with the other mill wastes in oxidation lagoons. The color is not appreciably decreased by such treatment.

Summary

Separation of suspended matter from the pulp and paper wastes can readily be accomplished. This form of treatment is satisfactory only if the solids removed from the water can be returned to the papermaking process or sufficiently low in quantity to be disposed of readily. Sludge disposal is indeed the major problem involved in reducing to a high degree the discharge of suspended matter to surface waters. In the case of many mills, clarification alone provides adequate treatment. An appreciable

oxygen demand reduction generally accompanies clarification since cellulose is readily decomposed under aerobic conditions.

Color removal is best accomplished by chemical precipitation methods. In the case of pulping and bleachery effluents, since the color is due mainly to lignin compounds in solution, settling or filtration does not result in appreciable removal. This is also the case with biological treatment for the lignins are not decomposed in the process. An important fact that should be considered in regard to assaying the color of wastes discharged from pulping processes is the fact that the lignins are to a degree acidity indicators varying from a pale yellow at low pH values to a dark brown at high pH values. Because of this effect, alkaline wastes high in color when measured on discharge may not cause as great a color rise as anticipated when neutralized by the normal acidity in the receiving stream. The reverse of this situation can occur in the case of acid wastes. Color imparted to surface waters by pulping wastes often assumes much greater importance in the public mind than it merits because of the fact that it is noticeable. The nature of the substances responsible for color in pulping waste are the same as those imparted naturally by decomposed vegetation.

Oxygen demand is a common problem occurring on the discharge of pulp and paper wastes and the one most difficult to overcome. This stems from the fact that cellulose and its degradation products and other products used in paper manufacture are readily decomposed by bacteria. This is particularly the case when sewage is discharged into a stream since it provides nutrients in the form of nitrogen and phosphorus compounds which the wastes are generally deficient in with regard to microbial decomposition. The application of sewage treatment methods for oxidizing these wastes are seldom applicable because of the plant size requirement in relation to the size of the manufacturing unit. In order to obtain broad application the efficiency of these processes must be greatly increased. Research is now directed toward this end.

Broader application of recovery methods and the development of new ones have and will continue to lead to substantial improvement in the oxygen demand discharged per unit of production. Other new techniques for reducing BOD values as well as by-product development will play an important part. The beneficial effect of better distribution of effluents into available receiving waters in reducing these problems is becoming better understood and appreciated.

Toxicity of pulping wastes to aquatic life appears from experimental work and field studies to be a very minor problem, difficulties occurring only under unusual conditions. It appears that fish kills attributed to toxicity have in many instances been due to oxygen depletion or other

causes. In the operation of kraft and soda mills toxicity represents more of a potential hazard than a problem, since while toxic materials are handled, few of them escape from the system during normal operation. Steps taken in most such mills to prevent toxic substances from reaching the effluent during process upsets, accidents or equipment failures have done much to reduce this hazard as have the recovery of by-products such as turpentine.

References

1. Allen, D. E., *Pulp and Paper*, 25, 56, (1951).
2. Barnes, G. B., Moggio, W. A., and Colmer, A. A., Louisiana State University Eng. Exp. Sta. Bull. Series No. 19 (1950).
3. Bibliography of Sulfite Waste Liquors, Institute of Paper Chemistry (1940).
4. Bibliography of Pulp and Papermaking in the U.S. and Patents Tappi.
5. Bloodgood, D. E., National Council for Stream Improvement, Research Bull. No. 7 (1947).
6. Bloodgood, D. E., National Council for Stream Improvement Technical Bull. No. 15 (1947).
7. Buswell and Sollo, *Sewage Works J.*
8. Chemical Abstracts.
9. Crawford, C. C., *Paper Mill News*, Sept. 7, 1946
10. Critical Reviews of the Literature, *Sewage and Industrial Wastes*
11. Eldridge, E. F., and Mallmann, W. L., Michigan Engineering Experiment Station Bull. No. 39 (1931).
12. Gehm, H. W., and Morgan, P. F., *Sewage Works Journal* 21, 851 (1949).
13. Holderby and Wiley, *Sewage Works J.* 18, 641 (1946)
14. Holderby, *Sewage Works J.* 18, 641 (1946).
15. Kessener, H. J., Report on Sewage Treatment in the Netherlands to the Health Organization Housing Commission, Geneva, Switzerland, 1938
16. Klason, *Papier Fabr.*, 7, 627, 671, 795 (1909)
17. Krancher, C. C., Annual Report No. 3, Strawboard Waste Research, Purdue University to National Council for Stream Improvement, Inc.
18. Lardieri, N. J., *Purdue University Engineering Bulletin*, Series 72, 296 (1949).
19. Logan and Heukelekian, *Sewage Works J.*, 20, 282 (1948).
20. Moggio, W. A., and Gehm, H. W., *Sewage and Industrial Wastes*, 22, 1326 (1950)
21. Moggio, W. A., National Council for Stream Improvement, Inc. Technical Bulletin No. 19 (1948).
22. Moggio, W. A., and Gehm, H. W., National Council for Stream Improvement, Inc., Technical Bulletin No. 31 (1950).
23. Moggio, W. A., "Chemical Treatment of Kraft Mill Wastes," Presented Tappi Annual Meeting (1951).
24. Morgan, P. F., National Council for Stream Improvement Technical Bulletin 22# (1948).
25. National Council for Stream Improvement Technical Bulletin #20 (1948).
26. National Council for Stream Improvement Technical Bulletin #8 (1947)
27. National Council for Stream Improvement Technical Bulletin #2 (1946).
28. National Council for Stream Improvement Technical Bulletin #24 (1949).
29. Porter, C. C., and Bishop, F. W., *Ind. Eng. Chem.* 42, 102 (1950)

30. Porter, C. C., Carpenter, C. H., Gehm, H. W., National Council for Stream Improvement Technical Bulletin No. 13 (1947).
31. Sulfite Waste Liquor Bibliography, Institute of Paper Chemistry.
32. Sutemeister, E., "The Chemistry of Pulp, and Papermaking," New York, John Wiley and Sons, Inc.
33. Swope, G., National Council for Stream Improvement Technical Bulletin No. 5 (1946).
34. "The Manufacture of Pulp and Paper," prepared under the direction of the Joint Executive Committee on Vocational Education representing the Pulp and Paper Industry of the United States and Canada. New York, McGraw-Hill Book Co.
35. Tyler and Gunter, *Sewage Works J.*, **20**, 709 (1948).
36. Tyler, *Sewage Works J.*, **14**, 835 (1942).
37. Tyler, Maske and Brewer, *Sewage Works J.*, **18**, 1155 (1916)
38. Van Horn, W. M., National Council for Stream Improvement Technical Bulletin No. 33 (1950).
39. Van Horn, W. M., National Council for Stream Improvement, Technical Bulletin No. 16 (1948).
40. Van Horn, W. M., National Council for Stream Improvement, Technical Bulletin No. 32 (1950).
41. Van Horn, W. M., Anderson, J. B., and Katz, M., *Trans. Am. Fisheries Soc.* p. 55 (1949).
42. Vogler, J. F., and Rudolfs, W., *Purdue Univ. Eng. Bull. Series 72*, 305 (1919)
43. Witham, G. S., Sr., "Modern Pulp and Papermaking," New York, Reinhold Publishing Corporation (1942).

11. Acid and Explosives Wastes

Robert P. Logan

Development Engineer, The Dorr Company, Inc., Stamford, Conn.

ACID WASTES

The common use of acid in chemical industries makes acid wastes one of the most widespread of all industrial wastes. Because of the similarity of the problem of treatment, alkaline wastes, however, are in the minority, and when encountered, other characteristics of the waste are often more troublesome than the alkalinity.

It is impossible to present flow sheets for the multitude of processes producing acid wastes. Wherever an acid is used or produced in a wet process an acid-type waste may result. Acid wastes requiring treatment are produced in the manufacture of TNT and nitrocellulose, rayon production, general chemical, agricultural chemicals, dyestuff and pharmaceutical manufacture, acid dipping and plating of nonferrous metals and the pickling of steel, petroleum manufacturing operations, certain textile operations and the drainage of abandoned coal mines. Wastes which are primarily organic but may require acid neutralization prior to biological treatment include those from the manufacture of antibiotics, yeast, alcohol, and certain cannery products. It appears that scarcely a wet industry exists which does not produce an acid waste.

The forms in which acid wastes may appear are as multitudinous as their sources. They may be simple dilute solutions of acids or mixtures of several acids. Mineral or organic acids may be encountered. Acids may present themselves in pure solutions, mixtures, or accompanied with suspended matter or highly dissolved salt concentrations. The acidity of the waste may be the major objectionable characteristic or it may be a minor part of the problem as when accompanied by high concentrations of dissolved organic matter or toxic agents.

Sulfuric acid is the most common mineral acid encountered. Hydrochloric and nitric acid are also found either alone or in company with sulfuric acid. Hydrofluoric acid may be present in certain metal-pickling wastes and phosphoric and acetic acids in some spent culture media from industrial fermentations.

In keeping with the varied sources and quality of acid wastes a wide range of concentrations may be found. Some acid wastes are discarded reactants, such as mixed acids from nitration processes and spent-metal pickle baths; others are wash waters or rinse waters containing traces of acids. The result is that wastes range in concentration from less than 0.5 to 25 per cent or more. The strength of the waste depends, to a large extent, on the volume of wash water used, which in turn depends on the nature of the product and the ease with which acid is removed. In addi-

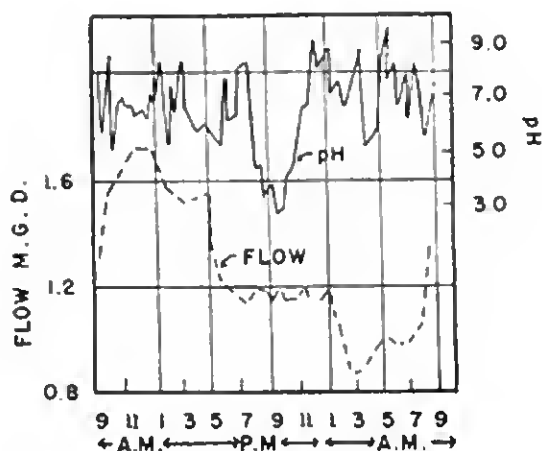


FIGURE 1. Variations in pH and flow

tion, admixture of other plant wastes and cooling waters with the acid wastes plays an important role in determining concentrations. With the infinite variety of sewer systems found in modern chemical plants it is evident that a wide range of acid concentrations may be found, even in wastes from similar processes.

An important characteristic found in many acid wastes is the extreme variation in acid concentration appearing in very short periods of time. This is especially evident where batch washing operations are conducted or where spent acid solutions are dumped periodically. In complex chemical manufacturing where operations are carried on for the production of a variety of products the same condition may result because of variations in the operations in different parts of the plant. Repetition of batch-wise operations may cause cyclic variations in acid content.

As an example of the variations which occur, Figure 1 shows the changes in pH of the waste from a large chemical manufacturing plant over a period of time. Such erratic characteristics introduce complications to the apparently simple problem of acid neutralization. They indicate the need for extremely rapid-response control equipment, a method of smoothing out the peaks of acidity and alkalinity, or a neutralization

process which is self-adjusting to the variations. Each approach may be singly or in combination with the others.

To further complicate the problem the buffering capacity of acid wastes vary, depending on the nature of the acids and salts present, and the pH of the waste does not alone give the complete picture; total acidity is of primary importance in calculating neutralization requirements and behavior of the waste under treatment.

Recovery of Waste Acids

The recovery of waste acids is a chemical engineering problem, which must be considered in connection with acid disposal. While complete acid recovery is not too often applicable there are instances where its use is the best solution to difficult problems. Frequently, it is cheaper to neutralize the waste than to recover the acid. Many technically feasible recovery methods are economically unsound, but complete or partial recovery may be economically justified in comparison with cost of treatment. The practicability of acid recovery also varies with chemical market conditions, geographical location of the industry and possible users of the recovered acid, the complexities of the manufacturing organization and the possibilities of re-use of recovered acid within the plant and other factors.

An instance of successful recovery is given by Weston²² who describes some of the achievements of the petroleum industry in the recovery of sulfuric acid from acid sludges produced in refining operations. He estimates that over one million tons of sulfuric acid are recovered annually from these sludges. One large refinery produces about fifty per cent of the total sulfuric acid used at the refinery from acid sludges. Weston describes two methods which are used: (1) Heating the acid sludge with water, causing two layers to be formed: one an oil layer and the other a solution of weak sulfuric acid which may be concentrated, allowing 40 to 70 per cent recovery of the acid; (2) A method involving the decomposition of the acid in the sludge in a 500°F kiln. The sulfur dioxide produced is converted to sulfuric acid in a contact acid plant, in which about 90 per cent of the acid may be recovered. The latter method is limited to larger refineries.

Another well established recovery method is the recovery of sodium hydroxide in the rayon industry. The impure caustic soda is separated from colloidal matter and dissolved impurities by the use of semipermeable, paper parchment membranes. Moritz¹¹ describes acid recovery methods used in France under dire economic necessity during the war. Some of the operations included recovery of sulfuric and hydrochloric acid from pickling liquor, from acid sludges of the petroleum industry,

from the production of oxalic acid, from the production of superphosphates and recoveries in the artificial fiber industry.

Remedial Measures

Certain remedial measures may be applied with beneficial results prior to actual treatment, or they may entirely obviate the necessity for treatment. Volume reduction, strength reduction, segregation, equalization, and interaction with other wastes may be desirable as pretreatment measures or may be necessary for adequate treatment of acid wastes.

Volume reduction is of importance where it simplifies the problem of neutralization. One million gallons of waste water containing 100 ppm of mineral acidity would contain the same weight of acid as 10,000 gallons of waste containing 10,000 ppm of mineral acidity, but the larger volume may be more difficult to treat than the smaller volume, requiring larger tanks and equipment and possibly the application of greater amounts of neutralizing agent. As a usual practice, acid wastes should be kept separate from large volumes of other wastes or cooling water as much as is practicable before treatment. Where existing sewer systems make this impossible it may be necessary to treat the acid waste at the source prior to its admixture with other wastes. Sometimes a certain degree of dilution may be necessary before neutralization can be successfully practiced. Additional valid reasons for keeping acid wastes separated from other wastes are that if the other wastes contain large quantities of suspended matter certain neutralization techniques are hindered, or if the other wastes contain organic matter and require biological treatment interference by the acidity of the acid wastes may develop. Volume reduction does not decrease the total amount of acid to be neutralized, but may contribute to the ease of treatment.

Process changes are often instrumental in accomplishing considerable reduction in the volume of acid wastes. The established principle of countercurrent operations needs no elaboration. Where this can be applied, as for example, in the countercurrent washing of acid-containing material, it will do much to reduce the total waste volume. Comparing countercurrent washing with batch washing another benefit results from the standpoint of waste treatment. The waste obtained tends to be more uniform in character than that obtained from batch operations.

Strength reduction, i.e., reduction of the total amount of acid in the waste, produces a positive and obvious benefit in economics of acid and neutralizing agent saved. Most obvious of the strength reduction methods is that of acid recovery. Wise^{2,3} states that 85 to 90 per cent of the acid in pickling wastes from brass and copper manufacture is found in the dilute wash waters. It reaches the wash water because of the "drag out"

resulting when the metal articles are removed from the concentrated acid pickle baths. Since the average acid usage in this industry is approximately 35 pounds per ton of metal it is apparent that a considerable amount of acid is wasted in dilute solutions. Any modification of process which would reduce the "drag out" aids materially in the reduction of strength of the acid waste. An adaptation of the drip saver used in the dairy industry may be suggested. The same principle would be of value wherever a product is passed through an acid bath whether it is a metal or textile.

Good plant housekeeping is automatic insofar as acid-using processes are concerned, but a more energetic pursuit of this type of plant maintenance may be beneficial in some cases. Spills, leaks, and drippage of acid should be kept to a minimum.

Equalization of Wastes

A valuable remedial measure is equalization. Variable concentrations of many acid wastes make their treatment difficult. If a constant feed machine is used to apply the neutralizing agent, periods will result when the waste is either over- or under-treated. Even with automatic pH controllers the variations may be so rapid as to introduce appreciable lag into the system. Accordingly, the treatment is less satisfactory and the cost is increased.

Equalization may be necessary even where the total amount of acid wasted is insufficient to damage stream life, sewers, or sewage treatment processes. Ellis² points out that average samples may show a non-lethal acidity over long periods of time, but that a slight increase in acidity to the lethal range for only a few minutes may kill fish in the stream for several miles below the factory effluent line. Similar conditions may develop where the factory effluent is discharged to municipal sewers with resultant damage to the treatment works.

A common misconception exists that adequate equalization will occur in an outfall line or in the municipal sewers due to the turbulence within these lines. Rudolfs¹³ has demonstrated that such is not always the case. Figure 2 compares the pH values taken at two manholes 3,000 feet apart in a municipal sewer. The upper manhole was just below a factory discharging a variable chemical waste. The time of flow between the two manholes was between 43 and 50 minutes depending upon the volume of flow. The curves indicate that the waste tended to flow in "slugs." Even when the flow of strong acid or alkali was of only a few minutes' duration the changes were evident at the lower manhole. Similar difficulties may be anticipated where long sewers are used to mix the neutralizing agent with the acid wastes unless the wastes are of a uniform character.

The advantages of equalization include utilization of alkalinity in the waste to assist in acid neutralization, economies of use of neutralizing agent, greater ease of control and more uniform distribution of waste to sewer or stream.

Methods employed for the equalization of acid chemical wastes vary from the use of lagoons of detention time measured in days to mechanically agitated equalization tanks with detention time measured in minutes.

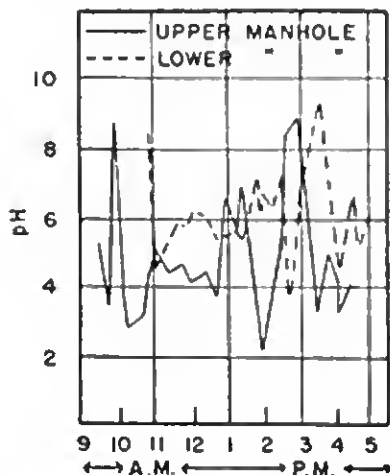


FIGURE 2. Illustration of waste movement in "slugs"

Large earth-bank lagoons are in common usage. One such installation¹⁰ with a total capacity of 12 million gallons, representing a detention time of approximately one-half day, is in use with a chemical waste of varied composition. Acidity is one of the objectionable characteristics. The compositing or equalization basin serves to even out the fluctuations in acidity of the waste before neutralization. No mixing devices or baffles are used in the basin. Equalization results from natural currents produced within the basin. This represents a crude but often satisfactory method of equalization. It has the advantage of simplicity and ease of maintenance. Its disadvantages are large space requirements and the fact that its purpose is often defeated by short circuiting or by density currents. The removal of suspended solids within such a lagoon is desirable from the standpoint of effluent quality. The problem of removing the sludge which accumulates over the years may be of considerable magnitude.

Smaller equalization tanks capable of holding a few hours' flow may also be used in some industries. They are particularly applicable where the process producing the waste is a batchwise procedure. In operations of this type the total time of a cycle may be several hours with the bulk of the acid being wasted in a relatively short time. A detention tank of sufficient capacity to hold the wastes from one cycle of the operation will

smooth out the unevenness of acid distribution to make the necessary treatment easier. Units of this type are sometimes operated batchwise in pairs.

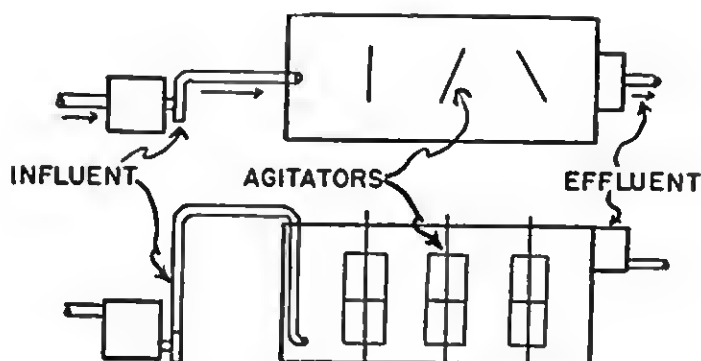


FIGURE 3. Layout of a typical equalization tank

The problem of still further reducing the size of detention tanks was studied by Rudolfs and Millar.¹⁶ A layout of the device developed by them is shown in Figure 3. The unit built was 27.5 feet long, 9.5 feet wide, and had a liquid depth of 10 feet, with a total capacity of 21,800 gallons, providing a theoretical time of 62 minutes. Introduction of the influent at the bottom of the tank aided in the prevention of solids deposition. Three wooden gate-type agitators were mounted vertically in the tank.

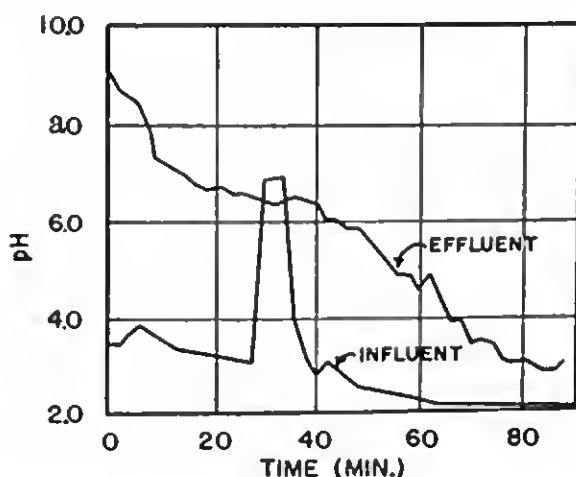


FIGURE 4. Relation between pH values and detention time with strong dose of alkaline material received

This device is designed primarily to eliminate momentary peaks in acidity or alkalinity. It is not intended to smooth out variations occurring over a period of time greater than the designed detention time of the unit. The authors state and prove mathematically that the method approaches a theoretically perfect equalization tank. They recommend it where:

- (1) Limited space is available for equalization.
- (2) It is not desired to settle out suspended solids.
- (3) Rapid fluctuations occur in the characteristics of the waste being treated.
- (4) Automatic control of subsequent treatment is desired.

They estimate that a 50 to 66 per cent saving in neutralizing agent resulted from the use of the equipment.

The over-all treatment provided by the waste treatment plant in which the accelerated equalization was incorporated has been described.¹⁶ Figure 4 demonstrates some of the results obtained. Although the equalization unit does not remove the major peaks it tends to reduce their magnitude considerable. Minor variations are effectively removed.

Volume, Character, and Strength of Acid Wastes

The great variety of processes producing acid wastes makes it difficult to use the usual methods of expressing volumes of waste in relation to units of product. A tabulation of some of the values reported is presented in Table 1. This will serve to emphasize the variation encountered as well as to illustrate the magnitude of flows found in various industries.

Effect of Acid Wastes on Sewers and Sewage Treatment Facilities

Acid wastes are damaging because of their nature. Sewerage systems are designed to conduct slightly alkaline sewage containing dissolved and light suspended organic matter to a sewage treatment plant. The treatment plant is designed to remove suspended solids by physical or chemical means and to stabilize organic matter by biochemical means. Acid wastes are particularly inimical to this design. They may do extensive damage to expensive collecting systems which are not designed for carrying acidic liquids, and may seriously interfere with the treatment for which the plant was designed.

The alkalinity of domestic sewage is largely dependent on the character of the water supply and seldom very high. A sewage with an alkalinity of 150 ppm is capable of absorbing about 120 pounds of sulfuric acid per million gallons. Any larger amount of sulfuric acid will cause the pH of the mixture to drop below 4.2 and mineral acidity will be present. If the pH remains that low for any protracted period of time serious corrosion of concrete will result.

All acids, mineral or organic, except oxalic acid, are corrosive to the type of cement and concrete used in sewer construction. Alkali hydroxides are stated to have no effect on Portland cement.⁵ However, they may decompose aluminous cements by dissolving the aluminum compounds.

TABLE 1. CHARACTERISTICS AND VOLUMES OF TYPICAL ACID WASTES

Waste	pH	Tot. Acidity as CaCO ₃	Alkalinity as CaCO ₃	Ingredients	Acids	Flow/gal/day	Ref.
Chemical laboratory	2.0-8.6	0-910 ppm	0-85 ppm	alkalies acids	H ₂ SO ₄ HCl	14,400-34,000	14
Plant waste	1.7-10.5	0-1,180	0-1,140	acids, alkalies, solvents, salts	HNO ₃ H ₂ SO ₄	865,000-1,800,000	14
Plant waste (Nitrocellulose)	0.9-1.4	9,000-11,800	0	solvents, acids	HNO ₃ H ₂ SO ₄	3,400,000-7,800,000	14
Plant Waste (General Chemical)	1.0-3.2	250-4,000	0	acids, salts, solvents	HCl H ₂ SO ₄	325,000-265,000	14
Plant waste	1.8-4.3	0-3,000	0-5,600	acids, alkalies	H ₂ SO ₄ HCl	90,000-160,000	14
Acid Dipping and Plating	1.9-4.4			acids, metals, grease oil, etc.	HCl HNO ₃ H ₂ SO ₄	28,800	24
TNT	2.4	485		wastes and cooling water		1,120,000/ 100,000 lbs TNT	21
TNT	1.2	3,460		no cooling water			21
Organic acid synthesis	1.9	2,450					
Yeast production	5.4	180		spent nutrients	H ₃ PO ₄ or NH ₄ (SO ₄) ₂	1,500,00 300,000	

Many municipalities, in setting up standards governing the quality of industrial wastes discharged to sewers, require that the wastes shall have a pH between 4.2 and 8.4, indicating that the wastes may have no mineral acidity or caustic alkalinity. In some cases even narrower limits are prescribed.

Secondary bacterial corrosion of sewers may be promoted by excessive acidities if ionized sulfides are also present in the sewage. The acidity of the sewage causes a greater volatilization of the sulfides as hydrogen sulfide, which in turn may be oxidized by certain bacteria growing on the damp walls of the sewer to sulfuric acid.

The possibility of interaction of the acid wastes with other industrial waste to produce toxic gases in the sewer atmosphere must also be recognized. Sulfides, cyanides, and sulfites will react in this manner.

Some difficulties reported¹² in England with acid wastes included damage to pumps and other equipment at the treatment plant. Increased odors at treatment plants due to volatilization of sulfides was also reported. Odors at sewage plants may become more than a local nuisance.

Acid sewages may promote the growth of undesirable growths in settling tanks and other plant appurtenances. This problem is of importance in trickling filters, where pH values of 4.0 to 5.0 may promote the growth of molds or wild yeasts with resultant clogging of the filter. At the same time the desirable organisms find conditions unsuitable and a poorer effluent is obtained.

The activated sludge process is also sensitive to low pH values. Values of pH lower than 6.0 have been found to be detrimental to the process. The sensitivity of sludge digestion of pH is well established. Definite retardation of the action will occur below pH 6.5. Sufficient liquid sewage may be collected with the sludge to produce this pH if the sewage is very acid. Rudolfs¹³ describes one large treatment plant at which the digestors were put out of operation by a sewage containing acid wastes. The pH of the sewage fluctuated between 2.5 and 9.6. Even after large quantities of lime had been added to the digestors to neutralize the acidity of the gas, production reached a value of less than 50 per cent of the normal amount.

Even where acid industrial wastes have been neutralized serious difficulties may develop when they are discharged to municipal sewers. In one instance, a chemical manufacturing company neutralized a large flow of acid wastes to prevent municipal sewer corrosion. Lime was used to treat the waste which contained considerable sulfuric acid. The neutralized waste contained calcium sulfate in excess of its solubility. No provision was made to remove this material and it passed into the city sewer. As a result the sewer became clogged with a dense, compact

deposit of calcium sulfate. Six weeks after it was cleaned out at a high cost to the manufacturing concern, the sewer was clogged again. This problem is more acute with low-grade sewers.

Effect of Acid Wastes on Streams

The concept of waste held by a chemical engineer may be entirely different than that held by the stream sanitarian. A striking example of this divergence of opinion is given by Ellis.² A large chemical plant using considerable quantities of sulfuric and nitric acids was able to account for 99.99 per cent of the acids used. From the viewpoint of the chemical engineer there was no waste. Yet the effluent from that plant reduced the pH of a stream to 4.0 for six miles below the plant. Aquatic life in this sector was killed. From the viewpoint of the stream sanitarian the acid wastage was very appreciable. It is too seldom appreciated that streams are poorly buffered and incapable of absorbing large quantities of acid without a drastic change in the pH value of the water. The amounts of river waters of various natural alkalinities required to neutralize various quantities of sulfuric acid with a resultant pH of 4.2 have been calculated and are shown graphically in Figure 5. The relatively low alkalinity of a stream can effectively neutralize only small quantities of acid. The pH need not be lowered to 4.2 before difficulties arise.

In speaking of aquatic life and industrial wastes fish are most commonly mentioned. Ellis² reports on the effect of acid and alkaline wastes on fish. Fish and aquatic life in general thrive best in waters with a pH range of 6.5 to 8.4. If the pH drops below 5.0 or rises above 9.0 fish may be killed or seriously handicapped. The actual pH value caused by the influx of acid wastes to the stream is probably of less importance than the magnitude of the change from the normal reaction of the water. Any change from the normal environmental conditions to which the fish are adapted may be detrimental. The gill structures of fish are most sensitive to acids. Ellis² lists the effect of acids on fish as follows: (a) impair the oxygen-absorbing power of the gills, (b) render useless certain excretory cells, (c) stop blood flow through the cells and thence to the vital organs, and (d) produce congested areas and stasis in the terminal portions of the gill filament. Alkaline waters damage the gills by dissolving protective mucous and by causing hemorrhages.

A pH of 4.0 may kill fresh water fish in a few minutes. However, it is not necessary to attain such a low pH to impair the activity of the fish. Other factors in the environment may increase the sensitivity of the fish to acids. If the water temperature is elevated or if the dissolved oxygen content of the water is decreased the fish are more susceptible to injury. probably because of the increased activity of the gill structures.

The killing of fish is only one of the catastrophes which may occur in a stream. All aquatic forms are in some way interdependent. Cycles of food utilization exist so that if one link of the chain is broken the succeeding forms must perish or leave the stricken area. Acid discharge, even though not fatal to fish, may destroy fish food and as a result the fish population declines.

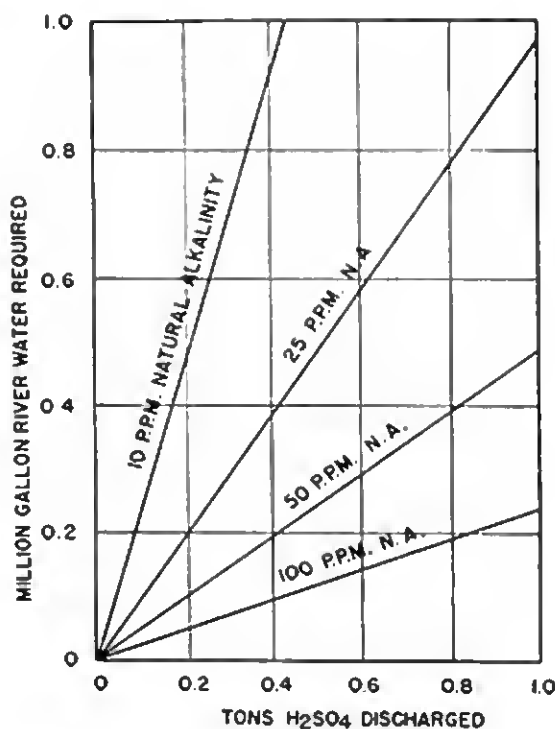


FIGURE 5. Amounts of river water of various alkalinity required to dilute H_2SO_4 and produce pH 4.2

The presence of high acid concentrations in streams may interfere with natural self-purification phenomena. In some cases the low pH, by preventing biochemical action, forestalls development of obnoxious conditions which would otherwise result on account of high organic pollution of the stream. This may appear to be beneficial, but really is merely a postponement of an evil. Chubb and Merkel¹ report that the zone of self-purification between a source of pollution and a point at which water is taken for municipal use was decreased from 60 miles to 20 miles because of acid conditions. Hence, the quality of the water was indirectly affected by the presence of acid farther upstream.

Water quality may be affected by acid wastes through the conversion of calcium and magnesium bicarbonates and carbonates in a stream to sulfates or chlorides. This represents an increase in the permanent hard-

ness of the stream and an increase in the cost of softening for industrial or municipal purposes.

Treatment

The neutralization of an acid with a base appears to be simple, yet, in the actual practice of acid-waste neutralization many difficulties arise.

The neutralizing agents available, all of which are used on occasion, are sodium hydroxide, sodium carbonate, ammonia, quick lime, hydrated lime and limestone in various grades. The limes and limestone are available as high-calcium or dolomitic materials.

Sodium hydroxide, sodium carbonate, and ammonia are satisfactory neutralizing agents. Their reactivity, ease of handling, and lack of sludge forming qualities, give them most desirable properties as neutralizing agents, but on account of their cost, these neutralizing agents are seldom used, except in cases where these chemicals are available as wastes. When their expense does not rule against them these agents may be used with any type of acid waste.

Where the use of a calcium or magnesium base is indicated the choice among the various bases will be determined by a number of factors. According to Jacobs⁹ the selection will depend on the type of acid, strength of acid, clarity of acid wastes, volume to be handled, available space for equipment, and relative cost per unit of calcium or magnesium in the neutralizing agents. These factors are important enough to warrant individual consideration.

The type of acid to be neutralized is important because of the behavior of the reaction products. In the case of hydrochloric and nitric acids the calcium salts of these acids have high solubilities and no difficulties are encountered regardless of the strength of acid being neutralized. Where sulfuric acid is to be neutralized the resultant product, calcium sulfate, has a limited solubility. If the solubility is exceeded a precipitate is formed which must be removed in separate sedimentation tanks, with an added sludge problem; or it must be passed out to the sewer with the possible danger of clogging the system. Another disadvantage is that calcium sulfate tends to coat the added particle of the neutralizing agent which results in losses of the neutralizing agent. The decrease of reactivity of the neutralizing agent requires longer contact periods with subsequent larger and more expensive installations.

Because of these difficulties the strength of waste acids, which are predominantly sulfuric acid, is of prime importance. Gehm⁴ and Jacobs⁹ have both recommended that sulfuric acid acidity be less than 5,000 ppm if limestone is to be used as the neutralizing agent, whether in the form of beds or by a feeding arrangement. At higher concentrations the pro-

tective covering of the sulfate reduces the effectiveness of the neutralizing agent. Rudolfs,¹⁵ working with a waste containing 16 per cent sulfuric acid and 14 per cent hydrochloric acid, found the following maximum acid concentration to be permissible if no sludge is to be formed:

Dolomitic hydrate	0.35%
75% Dolomitic hydrate and 25% sodium carbonate	0.45%

Much lower concentrations were allowable when calcium hydrate or calcium quicklime was used.

The same worker made the observation that the quality as well as the quantity of sludge varies with the nature of the neutralizing agent. Calcium carbonate produces a heavy, granular, rapid-settling sludge. Hydrated high-calcium lime produces a flocculent and voluminous sludge. A very finely divided microcrystalline precipitate is obtained with dolomitic hydrate. These properties may be put to good use depending on whether the waste is to be settled following neutralization or whether an attempt is to be made to pass the unsettled waste directly to the sewer or stream.

Both Gehm³ and Rudolfs¹⁵ believe that calcium sulfate will form a supersaturated solution if the dilution is high enough. At higher dilutions the calcium sulfate tends to remain supersaturated for a time and if it does precipitate it forms a finely divided, easily suspendible precipitate. On the other hand, if the acid is too concentrated the calcium sulfate forms in large rapidly-settling masses.

Various means of reducing sludge volumes are discussed by Rudolfs^{13,14}; the combination of dolomitic hydrate and sodium carbonate is considered especially effective from the standpoint of both sludge production and cost.

The clarity of the acid waste being treated is usually of importance only when the wastes are being treated by passing downward through limestone beds. The stone acts as a filter and may clog rapidly and become ineffective if the suspended solids content of the waste is too high. The difficulty can be obviated by the use of up-flow neutralizers described below.

The volumes of waste to be handled and space available for equipment are factors which should be considered together. If ample space is available lagoons may be used for compositing and removal of insoluble products of reaction. If space is at a premium it may be necessary to resort to accelerated equalization and mechanically cleaned sedimentation tanks for solids removal.

The choice of neutralizing agents as well as equipment may be deter-

mined by factors of volume and available space. If the volume is very small and space must be conserved, the use of sodium carbonate, sodium hydroxide, or ammonia may be indicated. The desirable features of these agents may offset their higher cost. When large quantities of waste are to be handled, combinations of dolomitic and high-calcium lime, or of dolomitic lime and sodium carbonate may be desirable, if minimum sludge handling facilities can be provided.

The final factor which should be considered is important in the economic sense. A criterion for determining the relative cost of the neutralizing agent is the basicity factor described by Hoak, *et al.*⁶ This factor as applied to lime and limestone represents the grams of CaO per gram of alkaline agent as determined by actual reaction of the agents with an acid rather than by usual chemical techniques. It is not sufficient to judge the relative costs of lime in their cost per unit weight alone. Hoak⁸ makes a comparison of delivered costs of some of these materials, indicating that dolomitic limes may have a distinct cost advantage over high-calcium limes. In addition, the sludge problem is decreased. The disadvantage of dolomitic lime is its lower rate of reaction, necessitating longer reaction time, or use of excess material. If a cheap supply of finely ground limestone is available greater economics are possible. The stone must be more finely ground than the usual commercial stone, otherwise its reactivity is too low. Other disadvantages are its tendency to foam and the difficulty of control because of carbon dioxide remaining in solution. It has been used successfully in large installations. Hoak⁷ discusses the possibility of using split treatment with limestone and lime for neutralization of pickle liquor, which would be applicable to simple acid wastes only when a pH above 7 is desired.

Equipment for Neutralizing Wastes

Other than equipment for pH control and chemical feeders there has been little standardization of acid neutralization equipment.¹⁷ This is probably a reflection of the diversity of problems encountered in this field of waste treatment. Most existing installations have been designed specifically for the job at hand. Because of this it is not possible to generalize about equipment; instead some descriptions of existing plants will be given.

King *et al.*¹⁰ describe the operation of a 20 mgd waste treatment plant at the Calco Chemical Company plant at Bound Brook, N. J. A chemical waste of complex composition is treated by collection, compositing in a large lagoon, neutralization, settling, and aeration. The waste is neutralized to pH 4.0 with a waste calcium carbonate slurry obtained from a near by magnesia manufacturing plant. The calcium carbonate

slurry is degritt and thickened to about 20 per cent consistency. The waste passes under a distributing channel from which the calcium carbonate is added. Control is automatic by a pH controller, actuating a diaphragm valve, which closes on a gum rubber tube conducting the neutralizing agent to the distributing channel. The calcium carbonate slurry is pumped at a constant rate. Any excess not passed by the gum tubing to the waste is recirculated to the thickener. Mixing of the slurry with the waste is aided by two vertically-mounted mixers. King reports the use of approximately 20 tons of calcium carbonate per day at this installation. A very slight after precipitation is stated to occur.

Jacobs⁹ describes two large neutralizing plants. The first uses ground limestone; as much as 400 tons of limestone per day were used during the war. The stone was stored in a silo and fed by means of three 9-inch screw conveyors of variable speed. These feeders were subject to control and could deliver from 40 to 240 pounds per minute. The stone dropped from the feeder to a standard Schutte and Koerting sand sluicer operated with water at 174 psi pressure. The slurry of water and stone was fed to the sewer carrying the acid wastes. The sewer lines provided 30 minute detentions and were sloped to provide a minimum velocity of 3 feet per second. This velocity prevented deposition of unreacted stone and sludge. The waste then entered a ditch and flowed one mile to a settling basin in which the sludge was removed. The settling basin dam spillway provided aeration which aided in carbon dioxide removal.

The other plant described by Jacobs was designed to treat a mixture of chlorine water, hydrochloric acid, and sulfuric acid with hydrated lime. Dilution was provided to reduce the sulfuric acid concentration to the point where calcium sulfate did not precipitate. The lime was fed from a storage bin by a lime-feeding device to a sand sluicer. The lime slurry, acid waste, and the diluting water were added together to a down-comer of the neutralization tank which provided a detention time of 2 minutes. Agitation was provided; control was by a pH controller actuating the feeder. If dolomitic hydrate is used the neutralization plant must be larger.

The treatment of acid wastes, the character of which is illustrated in Figure 1, is described by Rudolfs.¹³

The plant comprised bar screens, wet well and pumps, flash mixers, equalization basin, and mixing tanks provided with agitators. Neutralization was with hydrated lime fed as a 10 per cent slurry and controlled by automatic pH apparatus. The neutralization effected an average pH change from 4.8 to 8.2. An average flow of 1.17 million gallons per day required 1,690 pounds of lime.

In general, pH control equipment is the only standardized equipment

used in acid neutralization. Automatic pH control apparatus is usually installed only where the stronger bases such as caustic soda or limes are being used. However, it has been recommended or used for limestone beds or where limestone slurry is fed.^{4,6} This equipment may be adopted, by means of control, to either dry chemical feeders or slurry feeders.

Sheen¹⁸ has described some of the factors which must be considered in using automatic pH control apparatus for acid neutralization. Perhaps,

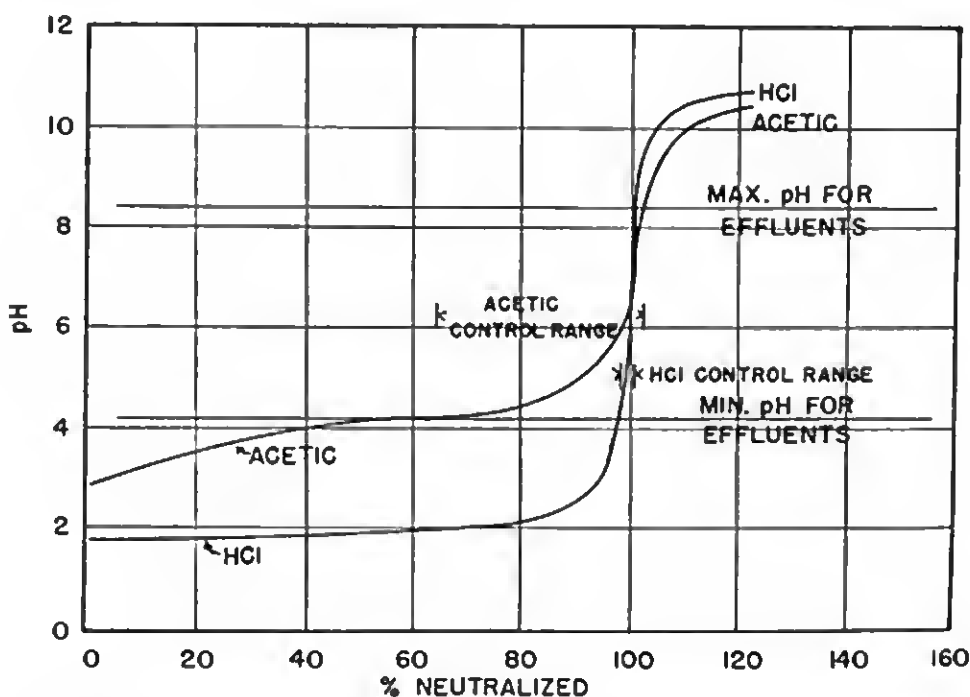


FIGURE 6. Characteristic titration curves of weak and strong acids

the most important factor is the quality of the acid waste being neutralized. If the waste has little or no buffering action pH control will be more difficult than if it is well buffered at the desired pH. This may be illustrated by Figure 6 which shows titration curves for a strong (hydrochloric) acid and a weak (acetic) acid. If the allowable pH range for the effluent from the neutralization of these acids is between pH 4.2 and pH 8.4 the control for the hydrochloric acid neutralization must be much more accurate than for acetic acid. While these are extreme cases, the same situation to a lesser degree will be encountered in actual operation, depending on the presence or absence of buffering salts and type of acid. If little buffer action is present Sheen recommends that an increased detention time be provided or that smaller increments of the alkali be added at one time. The less the slope of the neutralization curve at the control point the lower the detention time required.

The pH control equipment must be capable of adjustment both for

the percentage of the full scale (pH range) over which the controller is to operate and for the rate of increase or decrease of the chemical feed. According to Sheen this is necessary to allow for variations of the buffer action and slope of neutralization curve, the detention time, the reaction time, rate and degree of change of characteristics of the raw waste, control point required, mixing, sampling, and temperature. Flow variations should also be integrated by the controller. This may be accomplished in a controlled-volume pump in which the variations of rate of flow would control the pump speed and the variation of pH would adjust the pump stroke volume. This type of pump cannot be applied to all types of neutralizing agents.

Limestone Beds

The use of limestone beds is recommended for many problems where the flow and amount of acid to be neutralized are small and treatment with a minimum of attendance is desired. The use of a limestone bed eliminates the need for control beyond the rate of feed of stone, provided the effluent pH may range from pH 4.2 to about 8.0. This range must be suitable because the actual effluent pH obtained is dependent on the amount of carbon dioxide remaining in solution from the neutralization reaction. A second requirement is that the waste must be low in suspended solids, although with up-flow beds this is of less importance.

Limestone beds may be of two types, down-flow and up-flow. Down-flow beds have a disadvantage in that suspended solids from the waste and inert materials remaining from the stone tend to accumulate and eventually cause clogging. Jacobs⁹ recommends that the acid content of the waste be less than 0.5 per cent and the rates of 0.5 to 1 gal/min/sq ft of bed area be used with a 5 foot bed.

Up-flow beds have an advantage in that the concentration of suspended solids in the waste is of minor importance, higher rates may be used, and installation size and space required reduced.

Gehm^{4,3} has reported on extensive studies with up-flow neutralizing beds. All factors affecting the operation were investigated thoroughly. No significant differences were found in operating characteristics between calcite stone and amorphous stone.

The relationship between bed depth and permissible rate of application was found to be a linear function. Applications of 15 gal/min/sq ft were possible through a bed of one-half foot and 115 gal/min/sq ft through a bed 3 feet deep.

The acidity of the waste is very important as shown in Figure 7. The concentration of 5,000 ppm or 0.5 per cent acidity again appears to be critical.

The stone size is of importance in determining the rate of application, because the activity of the stone is determined by its surface area; therefore, the permissible rate increases rapidly as the stone size decreases.

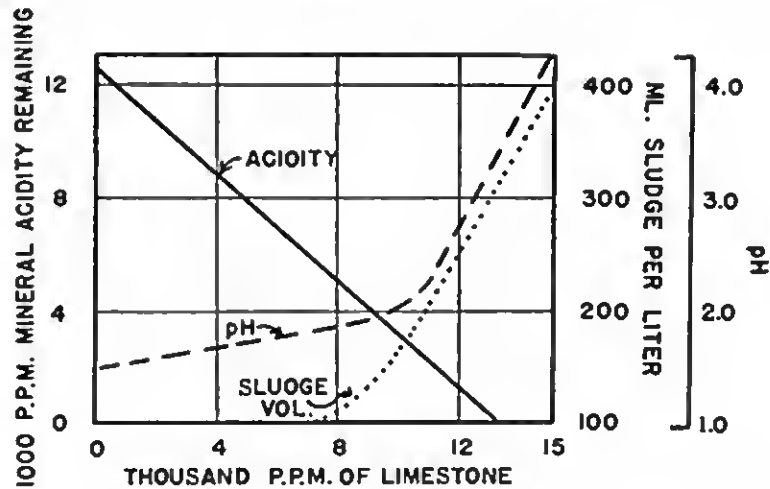


FIGURE 7. Neutralization of nitro-cellulose waste with high-calcium limestone

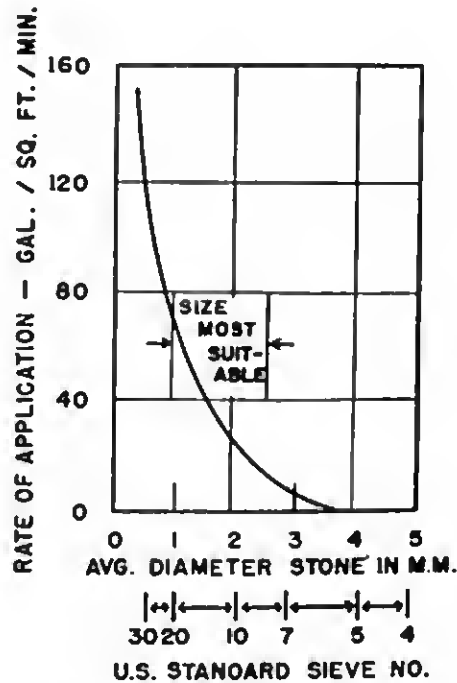


FIGURE 8. Effect of stone size on rate of application of nitro-cellulose waste

The allowable rates obtained in a waste containing 4,250 ppm of mineral acidity are shown in Figure 8. Stone of less than 1-mm size tended to wash out too easily. Stone larger than 2.5 mm tended to be too unreactive. It is recommended that stone in the range of 7 to 30 mesh be used.

Gehm believes that application rates of greater than 20 and less than 80 gal/min/sq ft should be used. The bed should be 2 to 4 feet deep and sufficient free board to allow for 100 per cent expansion.

One of his proposed designs⁴ is illustrated in Figure 10. This installation would be capable of handling 100,000 gallons per day of nitrocellulose waste of 10,000 to 15,000 ppm of mineral acidity. Dilution with an equal amount of water is proposed.

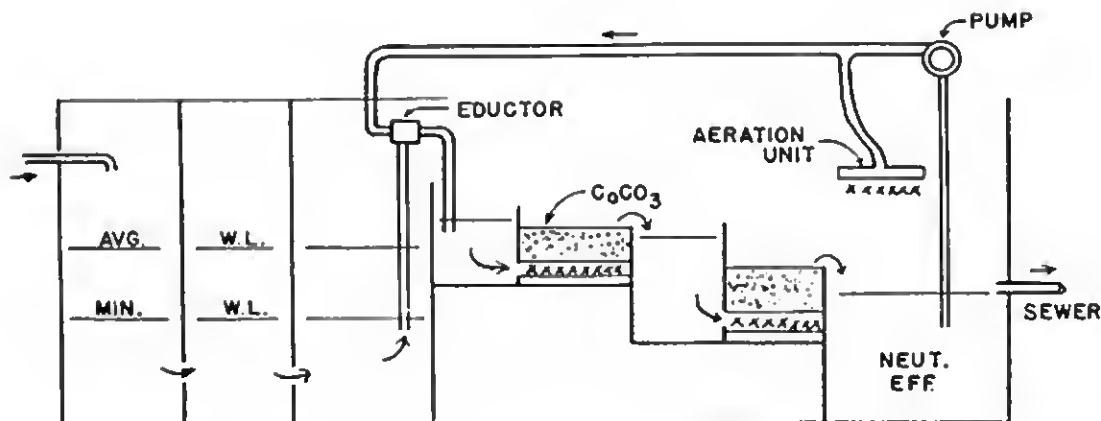


FIGURE 9. Up-flow limestone bed on tile support²¹

McNicholas¹² describes a compact double bed up-flow neutralizer. This unit was constructed under a truck driveway so that no valuable space was used. The plant treated a relatively low flow of 200 gal/min of plating iron wastes with pH values ranging from 1.9 to 4.4. Some of the waste is recirculated through the limestone beds and provision is made for spray aeration for CO₂ removal. No attendance is required at this plant other than adding the limestone through gratings into the beds as the stone is consumed.

Up-flow limestone beds appear to be ideally suited where relatively small volumes of waste are to be treated with a minimum of expense and maintenance of equipment.

EXPLOSIVES WASTES

Waste problems from the manufacture of explosives and munitions are mostly local. The chief forms of explosives produced are trinitrotoluene (TNT), smokeless powder, nitroglycerine and smaller amounts of sensitive priming agents used in fuses, caps and other devices.

TNT

The nitration of toluol is accomplished in three stages to produce mono-, di-, and trinitrotoluenes. The impure nitrated product is washed

free of acid and crystallized. The removal of isomeric TNT's and water-soluble sulfonates is accomplished with sodium sulfite and washing.

The liquid wastes have three components: (a) acid wash waters from washing of TNT after nitration, (b) red water or sellite waste from sulfite treatment, and (c) cooling waters.¹⁹

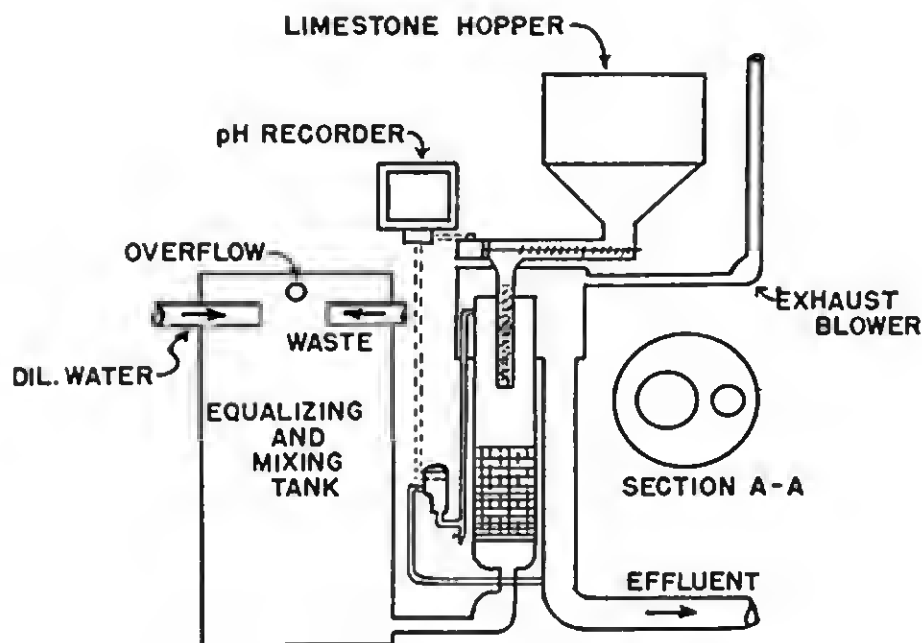


FIGURE 10. Typical up-flow neutralizing bed

A survey of three TNT plants showed that pH values of the waste varied from 2.4 to 2.7 and without cooling water averaged 1.2. The wastes have a yellow-to-red color and considerable odor. Average analytical results are shown in Table 2.

TABLE 2

Plant	Color (ppm)	Odor Conc.	Acidity (ppm)	NO ₂ (ppm)	NO ₃ (ppm)	SO ₄ (ppm)	Tot. Sol. (ppm)	Susp. Sol. (ppm)	O.C. (ppm)
A	7,100	70	291	15	107	672	2,277	166	795
B	6,300	16	134	20	—	604	1,991	29	551
C*	34,000	11	3,230	62	310	2,923	10,175	17	1,057

*Without cooling water.

About half of the total solids are volatile.

Powder

Smokeless powder is manufactured from purified cotton linters using H₂SO₄, HNO₃, alcohol, ether and smaller amounts of diphenylamine as stabilizer. NaOH or Na₂CO₃ is used as neutralizing agent. The solvents

are recovered. The waste consists primarily of a mixture of acids with small quantities of suspended materials, and aniline from the manufacture of the diphenylamine (Table 3). Some recovery is practiced on the "white water" produced by boiling and poaching of the cotton linters.

Nitroglycerine

Production of nitroglycerine involves the nitrification of glycerine with H_2SO_4 and HNO_3 . The mixture is separated with the nitroglycerine rising to the top as an oily liquid. The oily liquid is washed with water and agitated with air, washed with weak Na_2CO_3 solution, and the clear yellow oil is stored in lead tanks.

TABLE 3. ANALYSES OF WASTE PER 100,000 POUNDS OF EXPLOSIVE (LBS)

	Smokeless Powder ¹	Nitroglycerine ²
H_2SO_4	100,000	5,100
Alkalinity (CaCO_3)		4,740
Sulfates	59,800	1,890
$\text{NO}_2\text{-N}$	108	211
$\text{NO}_3\text{-N}$	25,500	5,740
O.C.	3,990	770
BOD	2,460	197
Total vol. sol.	91,000	8,070
Suspended solids	3,750	318
Hardness (CaCO_3)	15,500	1,440
Pop. equivalent	14,500	1,158
Flow (mg.)	5.37	2.76

The character of the waste is shown in Table 3. It is evident that the waste, for equal quantities of product, in terms of pollutional matter is greatest for the smokeless powder production.

Effect on Streams

The high acidity of some of these wastes has a deleterious effect on streams by upsetting the natural balance of stream ecology. The BOD of the wastes is comparatively low, but even with neutralization, the high nitrate concentration may cause excessive growth of algae. When the receiving stream is used as a water supply for domestic or industrial purposes, the color, taste and odor of some of the wastes are of particular importance.

Treatment

Neutralization of the acid explosives wastes with dolomitic lime is effective. Chemical treatment, or ozonation, for removal of oxygen con-

suming materials is ineffective. Experiments to determine the effect of activated carbon showed that only about 30 per cent of the oxygen-consuming materials could be removed at a high cost. Reduction of nitro compounds by electrolytic methods to reduce color is feasible, but the material is not amenable to biological treatment. The best solvent extraction method reduced color from 120,000 to 37,000. Chlorination to remove color in the order of 5 to 20 ppm reduced color 25 to 50 per cent. Bromination was about twice as effective.

The sodium salts of nitrotoluene sulfonic acids cannot be oxidized biochemically and purification cannot be expected in streams. Wastes mixed with sewage can be tolerated to a certain extent by biological treatment methods, but as little as 5 per cent TNT waste affects BOD reduction of the activated sludge process.

References

1. Chubb, R. S., and Merkel, P. P., *Sewage Works J.*, **18**, 692 (1946).
2. Ellis, M. M., *Proc. First Ind. Waste Conf. Purdue Univ.* (1944).
3. Gehm, H. W., *Sewage Works J.*, **16**, 104 (1944).
4. Gehm, H. W., *Chem. & Met. Eng.*, p. 124 (Oct., 1944).
5. Hammerton, C., *Proc. Inst. Sew. Purif. (England)*, 150 (1944).
6. Hoak, R. D., Lewis, C. J., and Hodge, W. W., *Ind. Eng. Chem.*, **36**, 274 (1944).
7. Hoak, R. D., *et al.*, *Ind. Eng. Chem.*, **37**, 553 (1945).
8. Hoak, R. D., *et al.*, *Ind. Eng. Chem.*, **39**, 131 (1947).
9. Jacobs, H. L., *Chem. Eng. Progress*, **43**, 5, 247 (1947).
10. King, V. L., Bean, C. H., and Lester, R. E., *Sewage Works J.*, **14**, 66 (1912).
11. Moritz, Rene, *Chim. Ind.*, **48**, 2, 72 (1942).
12. McNicholas, J., *Surveyor*, **95**, 459 (1939).
13. Rudolfs, W., *Sewage Works J.*, **15**, 48 (1943).
14. Rudolfs, W., *Ind. Eng. Chem.*, **35**, 227 (1943).
15. Rudolfs, W., and Rudolfs, W., Jr., *Public Works*, **24** (1944).
16. Rudolfs, W., and Millar, J. N., *Sewage Works J.*, **18**, 686 (1946).
17. Rudolfs, W., "Lime Handling, Application and Storage," *Nat. Lime Assoc., Washington, D.C., Bulletin* 213.
18. Sheen, R. T., *Ind. Eng. Chem.*, **39**, 1433 (1947).
19. Schott, S., Ruchhoft, C. C., and Megregian, S., *Ind. Eng. Chem.*, **35**, 1122 (1943).
20. Smith, R. S., and Walker, W. W., *Pub. Health Rpts.*, **58**, 1404 (1943).
21. Smith, R. S., and Walker, W. W., *Pub. Health Rpts.*, **58**, 1365, 1373, 1393, 1409 (1943).
22. Weston, R. F., *Proc. First Ind. Waste Conf. Purdue Univ.* (1944).
23. Wise, W. S., *Proc. First Ind. Waste Conf. Purdue Univ.* (1944).
24. Reidl, A. L., *Chem. Eng.*, p. 100 (July, 1947).

12. Steel Pickling

Richard D. Hoak

Senior Fellow, Mellon Institute, Pittsburgh, Pa.

The removal of oxide scale from certain steel products prior to further processing is an important manufacturing step. For many reasons the operation is an essential one and the practice is widespread, both at steel mills and at fabricating plants. Such major products as sheets, strip, wire and galvanized pipe are suitably treated for the purpose by immersion in an acid bath for a relatively brief period. This process is called "pickling" and, as it proceeds, the dissolution of part of the scale and some of the base metal results in the accumulation of iron salt in the bath. Eventually the pickling liquor loses its effectiveness and must be discarded; disposal of this liquor has been a problem for many years.

A variety of acids (sulfuric, hydrochloric, nitric, hydrofluoric, phosphoric, individually and in combination) is employed, depending on the kind of product being treated; but sulfuric acid accounts for more than 90 per cent of the tonnage pickled, and the steel industry is primarily concerned with methods for handling sulfate liquors.

Steel is pickled in both batch and continuous equipment. In the former, the products are suspended in an acid bath, with or without agitation, until pickling is complete; the time of immersion varies from about ten minutes to an hour or more. The spent liquor usually contains from 0.5 to 2 per cent of free acid and 15 to 22 per cent ferrous sulfate, as FeSO_4 . In continuous pickling, steel strip from a coil passes through a scale-breaker, an automatic welder or stitcher where a fresh coil can be joined to the strip ahead, a series of tanks containing pickling liquor, a rinsing device and a drier; finally it is re-coiled. The rate of passage of the strip is such that the total pickling time per unit area is approximately one minute. The waste liquor from a continuous pickler generally averages 4 to 7 per cent free acid and 14 to 16 per cent ferrous sulfate.

The tonnage of steel products that require pickling has increased rapidly. From a production in the United States of less than 1,000 tons of tin, terne and black plate in 1891, the industry had grown to manu-

facture 6,171,726 tons of these products in 1952. In the same year 13,230,888 net tons of full finished sheets, strip and flat galvanized products were made.² An accurate estimate of the volume of spent pickle liquor produced in these operations is difficult to obtain, but it is probably in excess of 600,000,000 gallons annually. The rapid growth of the industry, which is still continuing, has contributed to the difficulty of reaching a satisfactory solution to the disposal problem.

DISPOSAL WITHOUT TREATMENT

Those concerned with stream pollution abatement prefer to discuss waste utilization rather than waste disposal, because such a term connotes a profitable process. In the case of spent pickle liquor, however, it has always seemed more appropriate to speak of its disposal because of the apparent unlikelihood that a universally practical recovery process would be developed. As a result, a number of methods have been used, or proposed, for disposing of spent liquors without treatment. These include discharge of the liquor into deep wells, fissures in cavernous limestone, abandoned mines, exhausted oil and gas sands, artificial lagoons, gravel sumps near large bodies of water, and sewers terminating in rivers, lakes or tidewater.

There are objections to each of these expedients. Wells and limestone fissures eventually refuse to accept more liquor through sealing of permeable strata by deposition of reaction products. Where the discharge reaches the underground water table, serious pollution often develops. Artificial lagoons, which depend on a combination of bottom seepage and solar evaporation, occupy valuable land area. Gravel sumps adjacent to large bodies of water have been used successfully, but the action of the liquor gradually seals the permeable area and new pits must be constructed frequently.

Where pickle liquor is discharged directly into streams or large bodies of water, the gradual oxidation of the iron it contains colors the receiving water brown in localized areas and makes them esthetically objectionable, even though the actual pollution effect may be relatively small in a particular instance. Complaints against this procedure led the steel industry to adopt other disposal expedients, of which the principal one is neutralization with lime or some other alkaline material. As a result, relatively little pickle liquor is now discharged directly to streams, except where they already carry a heavy burden of other wastes, especially acid mine water.

NEUTRALIZATION

Treatment of spent pickle liquor with an alkaline material, usually lime, to neutralize the free acid and precipitate the iron is practiced

widely in the steel industry. Although many processes have been proposed for recovering useful by-products from pickle liquor, only the manufacture of copperas, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, has been adopted commercially. The complex nature of steel mill economy militates against the successful operation of most recovery processes, and it is only at the largest completely integrated mills that by-product recovery is likely to be practical. It is a reasonable certainty that the relatively small producer of spent pickle liquor, except for unusual local situations, will have no alternative available but neutralization.

Where the community in which the mill is located has a sewage treatment plant, it is sometimes advantageous to enter an agreement with the municipality whereby the spent liquor can be discharged to the sanitary sewer system. This disposal method has been used in a number of instances to the mutual benefit of both parties. Ferrous sulfate is a good coagulant for sewage and it improves clarification in the primary settling tanks; indeed, copperas and lime comprise one of the accepted methods for chemical treatment of sewage. On the other hand, the mill can dispose of its liquor at low cost. There are, however, a number of factors that must be considered where this disposal expedient is contemplated.

It is necessary to neutralize the free acid in the liquor to prevent corrosion of sewers and sewage plant equipment. Neutralization of the free acid is also required to raise the pH of the liquor high enough for the ferrous iron to precipitate in the sewage stream. Although domestic sewage is slightly alkaline, its alkalinity is normally inadequate to neutralize more than a small proportion of raw pickle liquor. Soda ash, despite its relatively high price, is generally used for this purpose because it is easy to apply, and because it avoids the danger of sludge deposits which sometimes block sewers where lime, which precipitates insoluble calcium sulfate, has been the neutralizing agent. It is desirable that the partly neutralized liquor be discharged at a uniform rate, preferably proportioned to the sewage flow, and installation of holding tanks at the mill is necessary to provide a regulated discharge. A steady flow of liquor aids the sewage plant operator to control his process, and it facilitates the addition of neutralizing agent at the mill. Disposal of pickle liquor with sewage affects the operation of the sewage works adversely by increasing the bulk of sludge that must be handled there. It frequently happens that sludge-drying beds are taxed to capacity, and acceptance of any considerable volume of pickle liquor would require that they be enlarged. Payment by the mill for the necessary increase in capacity at the sewage plant may be sound long-term economy. Finally, pickle liquor cannot be treated in a sewage plant that uses the activated sludge process because iron in sewage clogs the air diffuser plates in activation tanks.

Complete treatment of pickle liquor with lime is costly because it yields

no saleable by-product, and, in addition, the resultant sludge frequently occupies almost as large a volume as the original liquor plus the lime slurry used in the treatment. The slurry from the neutralization plant is generally stored in lagoons, where bottom seepage and solar evaporation gradually reduce the volume of water in the sludge. The over-all cost of lime neutralization will range from \$10 to \$20 per 2,000 lbs of acid charged to the picklers; if space is not available for lagooning the slurry the cost may be much higher. The expense of neutralization, and the extensiveness of its present and future use, dictate the necessity for operating the process with the greatest economy consistent with a satisfactory degree of treatment. Efficient treatment will result from the application of certain basic principles described in the following sections.

Basicity Factors and Acid Values¹²

The basicity factor of an alkaline agent is a measure of the available alkalinity of the agent that avoids dependence on chemical analysis. This factor is of particular utility in evaluating the available alkalinity of limes, limestones and related materials, because chemical analysis of these substances is time-consuming and the results give limited information about their reactivity. The numerical value of the basicity factors cited here represents the grams of equivalent calcium oxide per gram of material. Where waste liquors are to be neutralized, the actual composition of the alkaline substance is not particularly important as long as its alkalinity can be related to some reference compound. Equivalent calcium oxide was chosen as the logical reference compound for pickle liquor treatment.

When limestone is calcined, some of the calcium and magnesium oxides may combine with silica, alumina and iron oxides to form compositions that are insoluble even in moderately concentrated acids; the neutralizing value of the substance is thereby reduced. On the other hand, certain complex calcium and magnesium silicates in limestone may decompose on calcination. Chemical analysis would not ordinarily distinguish between the available and unavailable alkaline components. The temperature of calcination and the particle size of the final product are important factors governing the availability of the neutralizing value of a lime.

The method for determining basicity factors reflects the value of the substance as a neutralizing agent under the conditions of use, and the procedure is quite simple. A sample of the material is heated with an excess of acid; after the proper interval of time the excess acid remaining is titrated, and the net acid consumed is calculated to grams of calcium oxide per gram of sample. The detailed procedure for lime follows.

Procedure. Using a weighing bottle, weigh accurately about 1.3 g of lime and transfer the sample to a small porcelain crucible. Place the

crucible upright in a 250-ml beaker containing 15 ml water. Cover the beaker, heat the water to boiling, and tip the crucible to fill it with the hot water. Allow to stand for several minutes to slake the lime completely. Scrub the crucible with a rubber policeman, wash and remove it, run in from a burette the quantity of 0.5*N* sulfuric acid required to react with the lime, then add 30 to 35 ml in excess. Wash the mixture into an Erlenmeyer flask, boil for 15 min., cool to room temperature, and titrate with 0.5*N* sodium hydroxide to a phenolphthalein end point. The boiling period suggested here is ample for most limes to develop their full basicity with sulfuric acid. The procedure for limestones is similar, except that a larger sample is used and the slaking step can be eliminated.

This method can be used with any common acid, and the choice of acid should be governed by the application intended. Basicity factors determined for a given boiling period will obviously vary with the same strengths of different acids and different strengths of the same acid unless the full basicity is obtained. In the procedure given above, it was desired to obtain the full basicity of the sample, but it is evident that the method provides means for establishing relative reactivities under any chosen set of conditions. Basicity factors for representative limestones, quicklimes and hydrated limes will approximate the values in Table 1.

TABLE 1. REPRESENTATIVE BASICITY FACTORS

Material	g CaO/g
High calcium limestone	0.49
High calcium quicklime	0.94
High calcium hydrate	0.71
Dolomitic limestone	0.56
Dolomitic quicklime	1.11
Dolomitic hydrate	0.92

Where the use of limestone is contemplated, the important relation between particle size and reaction rate must be recognized, and this is illustrated by the data in Table 2. In each case, samples of high quality 30-mesh high calcium limestone were ground until the whole sample passed a particular screen.

Acid Value¹²

Calcium hydroxide (slaked or hydrated lime) is only slightly soluble in water, but that which dissolves is completely ionized to calcium and hydroxyl ions. When lime slurry is mixed with pickle liquor the hydroxyl ions combine rapidly with hydrogen and/or iron ions, permitting more lime to dissolve. For every hydroxyl ion that reacts, an equivalent amount of calcium sulfate is formed; this compound largely precipitates, due to

TABLE 2. EFFECT OF PARTICLE SIZE ON REACTIVITY OF LIMESTONE

Boiling Time (hrs)	Basicity Factors of Samples Ground to Pass Mesh No.				
	30	65	80	100	200
1/2	0.4443	0.4572	0.4798	0.4874	0.5231
1	0.4571	0.4879	0.5030	0.5153	
1 1/2	0.4736	0.5088	0.5170	0.5244	
2	0.4855	0.5211	0.5229		
2 1/2		0.5249			
3	0.4958				

its limited solubility. Complete treatment of pickle liquor by neutralization may therefore be considered to be a union of calcium and sulfate ions to form calcium sulfate. To compute the amount of alkaline agent required to neutralize a given quantity of the liquor, it is thus necessary to know only its total sulfate content.

Accurate chemical analysis of pickle liquor requires considerable time, but its acid value, or total sulfate content, can be determined with an accuracy of 0.2 per cent in 15 to 20 minutes by a rather simple procedure.

Procedure. Pipette accurately 5 ml of the sulfate liquor into 50 ml of distilled water in a 250 ml beaker. Run in from a burette 25 to 30 ml of 0.5*N* sodium hydroxide in excess of that required for complete reaction. Heat to boiling for 2 to 3 minutes, stirring to avoid loss by bumping. Prepare a filter by placing a No. 42 Whatman (or equivalent) filter paper in a small Büchner funnel, moisten, and apply vacuum. Pour about 10 ml of a thin slurry of acid-washed asbestos on the filter, and rotate the funnel rapidly to throw the fibers to the edges of the paper to form a good seal. Turn off vacuum and pour the boiling mixture on the filter. Immediately begin applying vacuum gradually, taking 15 to 20 seconds to turn it on full to prevent the finely-divided precipitate from passing the filter.* Wash the residue with four 10 ml portions of water; this will usually be sufficient to recover all of the excess sodium hydroxide, but the final wash may be tested for alkali with phenolphthalein paper. Add a few drops of phenolphthalein indicator solution and titrate with 0.5*N* sulfuric acid to disappearance of the pink color.

Basicity Factor-Acid Value Nomograph¹²

The nomograph shown in Figure 1 provides means for the rapid estimation of the amount of alkaline material required for complete treatment of a given pickle liquor. It was constructed on the assumption that the agitation would be adequate to insure attainment of the full basicity of

* Alternatively, the mixture may be washed into a 100-ml volumetric flask, cooled to 25°C, filled to the mark with distilled water, mixed, and allowed to settle. A 50-ml aliquot is pipetted to a flask for back-titration.

the neutralizing agent under the conditions for which the basicity was determined.

For various reasons, the reaction of pickle liquor with an alkaline agent is quite complex, and the pH of a slurry of lime and pickle liquor is an unsatisfactory indicator of completion of the reaction. It is more or less customary in industry to add milk of lime to pickle liquor until a sample

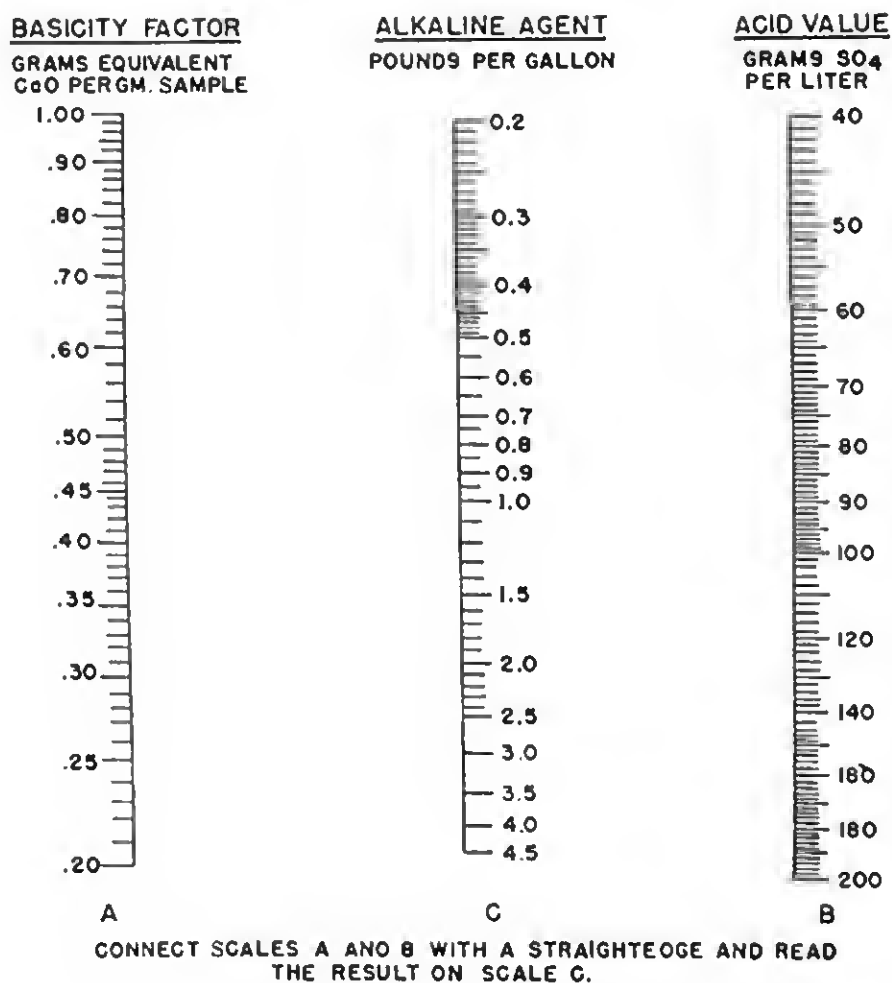


FIGURE 1. Nomograph for acid-waste treatment

of the slurry is alkaline-to-phenolphthalein. This procedure may result in under- or over-treatment, depending on the rate of lime addition, degree of agitation, strength of the liquor, temperature, reactivity of the lime, and other factors. The best way to insure complete treatment with maximum lime efficiency is to use the basicity factor-acid value relation. The economics of pickle liquor neutralization are dealt with later in this chapter.

High Calcium Lime Treatment¹³

The alkaline agent most commonly used for pickle liquor neutralization is high calcium lime, either as quicklime or as the hydrate. This material is highly reactive, and it is usually available in quantity near centers of steel manufacture.

Local conditions are so variable that only general principles of design can be given for any waste treatment plant, but conventional lime neutralization involves no problems of design or operation. All that is required in the plant itself is an acid-proof reaction tank equipped with an agitator, and equipment for slaking, screening and feeding quicklime to the pickle liquor. Neither quicklime nor hydrate can be added dry to pickle liquor without sacrificing a large proportion of their alkalinity. Hydrated lime must be suspended in water, but screening is unnecessary. In addition to the treatment plant, there must be provision for disposing of the sludge, and lagoons are generally used for the purpose.

Pickle liquor is usually treated in batches of convenient size. Liquor dumping schedules at the mill are governed by the rate of operation and the type of steel being pickled. The neutralization plant should therefore be provided with adequate pickle liquor storage tanks for protection against contingencies. Ample storage for the liquor also has the advantage of averaging its composition, thereby simplifying the neutralization operation. The discharge pipe from the storage tank should be protected by a screen to prevent refuse from damaging pumps.

Rinse water at the mill should be held to the smallest possible volume consistent with satisfactory results. This is especially important in the infrequent cases where rinse waters, as well as the strong liquor, must be treated. In such instances careless use of rinse water may necessitate the installation of a neutralization plant several times as large as would otherwise be required. In many localities it may be feasible to discharge rinse waters untreated, and, in such cases, the more dilute they are the better. Where rinse waters are large in volume, and must be treated, it may be good economy to handle them separately from the strong liquor. Collection of pickle liquor from several scattered operations to permit their treatment in a single neutralization plant may well represent the major capital cost of the treatment, and careful consideration should be given to plant location, segregation of strong from weak liquors, and reduction of rinse water volume, before a decision is reached.

The size and structural details of the pickle liquor neutralization tank will depend to some extent on local factors. The reaction tank must be acid-proof, and of sufficient size to hold a normal batch of liquor plus the lime slurry required; a safe freeboard should be included in the calculation of capacity. Where the daily volume of liquor is large, it will normally

be advantageous to use two or more tanks in rotation to reduce down-time. One or two combination lime slaking and storage tanks may be used, depending on needs. Lime tanks should have agitators, and should be calibrated to permit drawing known volumes of milk of lime; a float indicator on a scale graduated in gallons per inch is satisfactory.

Lime purchased from a manufacturer will usually be of reasonably constant quality, but where a jobber is the supplier shipments may not always come from the same source. In any case, representative samples should be analyzed at sufficiently frequent intervals to insure that the weight of available alkalinity per unit volume of milk of lime is always known with adequate accuracy. Analysis of each shipment also serves the purpose of guaranteeing that the lime meets with the specifications of the contract. When the analysis is known, a quantity of lime should be slaked to yield a milk of the proper density when diluted to volume in the lime tank. Lime should be slaked in the least amount of water, preferably warm, that will produce a heavy slurry, so that the maximum slaking temperature will be developed; too much or too little water during slaking will reduce its reactivity. When slaking is complete (15 to 30 min.), the slurry should be diluted with five or more pounds of water per pound of lime slaked. The milk is then ready for use, but it should be discharged to the treatment tank through a screen to remove unburned stone and coarse grit.

For the treatment of the pickle liquor, an appropriate batch of liquor, preferably hot, is drawn to the neutralization tank and the volume of lime milk, determined from the basicity factor-acid value relation, is run in at a moderate rate while the mixture is agitated vigorously. The reaction proceeds rapidly to completion; after all the lime has been added, mixing should continue for 15 to 30 minutes, depending on the reactivity of the lime.

The treated slurry is discharged to a storage lagoon. Design of the lagoon will depend principally on the land area available. Usually it will not be practical to install a weir, or other device, to draw off supernatant liquor because most slurries produced conventionally settle too slowly to justify this added expense. Where a suitable site for a lagoon is not available the difficulty can sometimes be overcome by constructing a relatively deep sump from which the heavy sludge is removed from time to time by dredging. In other cases it may be necessary to carry the slurry by pipeline or by tank car to a disposal area. Sludge disposal is often quite costly, especially where the mill is located in a built-up metropolitan district.

Slurries produced by the conventional neutralization practice just described cannot be efficiently dewatered by filtration or centrifugation. Re-

cent pilot plant work³⁰ has indicated an advantage in adding the spent pickle to the lime slurry, instead of the reverse. Recirculation of the mixture through a centrifugal pump until the reaction is completed produced a slurry that could be satisfactorily dewatered on a rotary vacuum filter. The same investigation disclosed that up to 75 per cent of the filtrate could be substituted for fresh water in slaking the lime. This use of filtrate improved slurry filterability and resulted in a substantial saving of water.

Dolomitic Lime Treatment¹⁴

Dolomitic lime is less reactive than high calcium, but it has a substantially higher basicity. The lower reactivity of dolomitic limes is due to the low solubility of magnesium oxide. This physical factor is augmented in the calcination of dolomitic limestone because calcium carbonate decomposes at a higher temperature than magnesium carbonate, and by the time the calcium carbonate has been completely calcined the magnesium oxide formed earlier is somewhat over-burned, thereby reducing its reactivity still further. The higher basicity of this compound is due to the lower combining weight of magnesium oxide. Basicity factors for dolomitic quicklimes are about 18 per cent higher than those for high calcium quicklimes, and about 28 per cent higher for the corresponding hydrates.

Using the quantity of dolomitic lime indicated by the basicity factor-acid value relation, 4 to 6 or more hours may be required for complete precipitation of the iron in pickle liquor. The reaction time can be reduced, however, by adding an excess of the agent; very roughly, and within limits, each 5 per cent excess reduces the reaction time about an hour. The reaction time can also be reduced by increasing the temperature; advantage of this factor can be taken in practice by treating the pickle liquor before it has had an opportunity to cool appreciably from pickling temperature (180 to 200°F). Increasing the rate of oxidation of the precipitated ferrous hydrate increases the reaction rate considerably; this effect can be achieved by introducing diffused air. Experimental work has shown that pickle liquor can be completely treated with dolomitic lime in about one hour if a 5 per cent excess is used, the liquor is treated hot, and aeration is provided.

The magnesium oxide component of dolomitic lime hydrates much more slowly than its calcium oxide fraction. For this reason it is desirable to allow slaked dolomitic lime to stand overnight before use.

With the above exception, the treatment of pickle liquor with dolomitic lime is the same as for high calcium lime. Dolomitic lime produces a bulkier sludge than high calcium. The sludge has a lower dry solids content, but it settles much more slowly. The basicity advantage of dolomitic lime

over high calcium places the two agents on a relatively equivalent basis for pickle liquor treatment. Where large volumes of liquor must be treated, the saving in cost of alkaline agent will permit the use of several expedients to reduce the reaction time without exceeding the cost for high calcium lime.

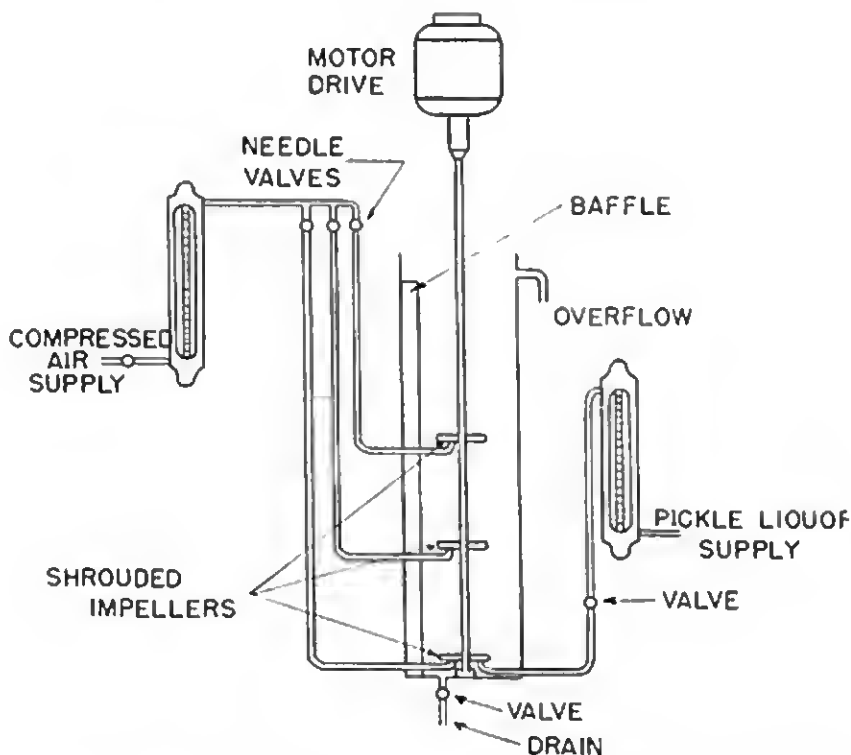


FIGURE 2. Diagrammatic sketch of reactor for new pickle liquor neutralization technique

A New Neutralization Technique¹⁶

The high cost of handling the large volume of sludge produced where pickle liquor is treated with lime by conventional methods directed research attention to the development of a process for reducing its volume or increasing its filterability. Both of these objectives were attained in the process described below.

Controlled oxidation to ferroso-ferric oxide of the ferrous hydrate that precipitates when pickle liquor is treated with an alkaline material, is the fundamental principle on which the process operates. Basically the process consists of feeding pickle liquor at a predetermined constant rate to an alkaline bath in a reactor, where the temperature is maintained above 75°C and means are provided for efficient aeration. A diagrammatic sketch of the reactor is given in Figure 2.

The basic principles of the process were established by using a cyclic

continuous method of operation, whereby pickle liquor was fed at a constant rate to a volume of slurry from a previous run, equal to about half the capacity of the reactor. Before the pickle liquor feed was started, the alkaline agent, equivalent to the volume of liquor it was planned to feed, was mixed with the slurry in the reactor. At the conclusion of a run the reactor was drained to its mid-point and a new cycle started immediately. This method was used because equipment was not available during development of the process for feeding alkaline agent at a uniform rate, but supplemental runs, where the alkaline material was added manually, showed that, with proper feeding devices, the process could be operated continuously without difficulty.

Successful operation of the process depends primarily on balancing the rate of iron precipitation with the rate of oxidation of ferrous hydrate. These rates must be so controlled that the iron in the precipitate will have a ferrie-ferrous ratio between 2 and 5, preferably between 2.5 and 3.5, while the temperature of the bath is maintained high enough to promote the formation of ferroso-ferrie oxide. Although many variables were considered in developing the process, experience showed that some were relatively unimportant and others were fixed by local conditions. In a commercial installation, provided the reactor includes means for efficient dispersion of air, the only variables to be considered are the rates of feed of pickle liquor and air, and the optimum excess of alkaline agent. These can readily be established by a few trial runs.

The process development work was based on two strengths of pickle liquor. One contained 60 g of Fe and 200 g of SO_4 per liter, representing the liquor discharged by continuous strip picklers; the other was exactly half that strength, to illustrate conditions to be expected where the strong liquor is diluted with rinse water. Table 3 gives the results of typical runs for magnesia, high calcium lime, and dolomitic lime with half- and full-strength pickle liquor.

TABLE 3. PICKLE LIQUOR NEUTRALIZATION BY NEW TECHNIQUE

Run*	Amount Agent, % Stoich.	P.L. Rate, ml/min.	Temp. (°C)	Slurry pH	Fe ⁺⁺⁺ Fe ⁺⁺	Fe in Sup't. g/l	Initial Settling, in./min.	Final Sludge Vol., % Orig.
MgO — half	105	270	80	6.9	3.36	0.03	0.85	8
MgO — full	104.5	117	80	7.4	2.69	0.04	0.53	16
HiC — half	105	285	79	9.0	2.53	0.00	0.58	35
HiC — full	105	140	82	9.5	2.50	0.00	0.40	58
Dol — half	110	108	84	8.0	3.45	0.01	0.78	20.5
Dol — full	110	75	82	6.9	2.53	0.02	0.60	30

*Represents magnesia, high calcium lime, and dolomitic lime, with half- and full-strength liquor.

The table shows that the supernatant liquors from magnesia and dolomitic lime treatment contained small amounts of soluble iron; this can be eliminated by continuing the air supply for a short time after the pickle liquor feed is stopped.

The table also discloses the interesting fact that the co-precipitated calcium sulfate accounts for the major portion of the sludge bulk. This may be seen by comparing the final sludge volumes for magnesia with those for the other two reagents. It should be noted that the sludge volume produced by full-strength liquor with high calcium lime was only 65 per cent greater than that from half-strength liquor; for dolomitic lime, the figure was 50 per cent. This shows the advantage in treating strong liquor by this process.

Only the initial settling rates are shown in the table. In all cases, sedimentation was complete in less than an hour, and in most runs in less than 15 minutes.

Filtration tests on the high calcium slurry, using a standard filter disk with an effective area of 0.1 square foot, showed a rate of 68 gallons of filtrate and 400 pounds of wet cake per square foot per hour. The wet cake averaged about 60 per cent dry solids. This filtration rate is approximately 20 times that of the slurry from conventional high calcium lime treatment. The filtration rate of dolomitic lime slurry was about one-third that of the high calcium rate. Filtration studies were not made on the magnesia slurry because its small volume would lend itself to separation in a sludge thickener.

This process offers a new approach to pickle liquor neutralization. It is being used commercially in a number of installations by steel fabricators.

Dry Lime Neutralization²¹

A neutralization procedure which uses dry lime has been developed through the pilot plant stage for shops producing no more than several thousand gallons of spent pickle per day. A 100 to 300 per cent excess of pulverized quicklime or hydrate is fed to the pickle liquor in a reactor equipped with an agitator. As the liquor is neutralized the excess lime forms a granular sludge that can be readily dewatered on a vacuum filter or in a basket centrifuge. Although this great excess of lime could not be justified for a large mill, the process may appeal to small plants because of its simplicity and the fact that the sludge need not be lagooned.

Limestone as a Neutralizing Agent¹³

Lime treatment of pickle liquor has been common for many years, but the development of processes using limestone for this purpose has

received scant attention. Limestone would appear to be a logical alkaline agent for pickle liquor treatment because of its wide geographical distribution and relatively low price. It has been used occasionally by permitting the liquor to percolate through beds of lump stone, but the results have usually been unsatisfactory. When sulfuric acid pickle liquor reacts with lump limestone, the deposit of a relatively impervious layer of calcium sulfate prevents the utilization of more than a fraction of its alkali-

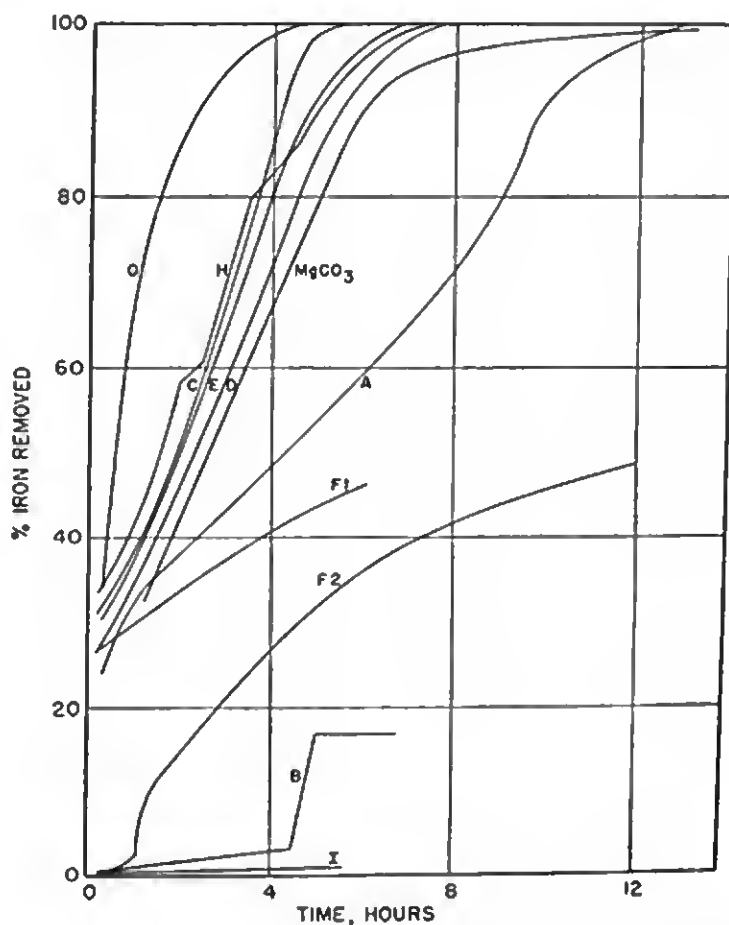


FIGURE 3. Rate of removal of iron from pickle liquor with pulverized limestone

linity. The upflow limestone process developed by Gehm⁹ for neutralizing acidic wastes is applicable to dilute pickle liquors and rinse water, but it is unlikely to be satisfactory for strong liquor because of clogging by the ferrous hydrate precipitate.

Pulverized limestone can be utilized much more effectively than lump or crushed stone because the fine particles tend to react more or less completely. Such material will quickly neutralize free acid and precipitate ferric iron in pickle liquor, but it will not precipitate ferrous iron completely, even if reduced to extreme fineness, because limestone cannot produce a sufficiently high pH. But the rate of oxidation of ferrous iron

increases rapidly with increasing pH, and, where oxygen can be supplied by aeration, many pulverized limestones will precipitate ferrous sulfate completely if the oxidation of the iron is allowed to go to substantial completion.

Pulverized limestones vary widely in their rate of reaction with pickle liquor. Reaction rates are governed by chemical analysis, fineness, and a specific reactivity, peculiar to each stone, that cannot be evaluated easily except by trial. The magnesium carbonate content of a limestone exerts a profound effect on its rate of reaction. Although many other factors affect its reactivity in some degree, the rate of reaction appears to be approximately inversely proportional to the quantity of magnesium carbonate it contains (above about 2 per cent). There is a critical particle size which varies with different limestones, but for most purposes the so-called mine-dusting grade, of which 80 to 85 per cent will pass 200 mesh, is satisfactory.

Table 4 gives the chemical analysis of a number of representative limestones, and Figure 3 shows their rate of reaction with a pickle liquor containing 63.8 g of Fe/l, and an acid value of 209.3 g SO_4 /l.

TABLE 4. ANALYSIS OF PULVERIZED LIMESTONES

Limestone	Loss at 150°C (%)	Acid insol. (%)	R_2O_3 (%)	CaCO_3 (%)	MgCO_3 (%)	Basicity Factor (gCaO/g)
A	0.17	0.73	1.09	93.90	2.26	0.554
B	0.11	0.35	0.49	51.28	44.31	0.600
C	0.00	1.20	0.49	95.33	0.75	0.537
D	0.10	5.60	1.31	87.35	1.05	0.493
E	0.06	0.94	0.29	96.97	0.79	0.554
F	0.13	1.64	0.38	86.97	10.89	0.561
G	0.10	2.21	0.50	96.91	1.17	0.547
H	0.08	2.35	0.41	95.10	1.50	0.547
I	0.08	3.72	0.68	51.81	42.62	0.576

The curves in Figure 3 illustrate clearly the effect of magnesium carbonate when it exceeds about 2 per cent in the limestone. The curve for U.S.P. magnesium carbonate indicates that it is the physical combination of the magnesium carbonate in limestone that affects its reactivity. The dashed line of Curve B indicates the addition of a 100 per cent excess of limestone. These data show that the low reactivity of most magnesium limestones make them useless for pickle liquor treatment. A dolomitic limestone has recently been found²⁰ that is superior to some high calcium stones in reaction with sulfuric acid; this has been ascribed to an uncommon crystal structure.

Limestone-Lime Split Treatment¹³

Although pulverized limestone alone will often require more time than can be allowed for complete treatment of pickle liquor, a combination of

this material with quicklime will sometimes permit an economy in operating costs. This method of treatment involves merely the addition of enough high calcium pulverized limestone to neutralize the free acid and precipitate the ferric iron, followed by lime slurry to complete the treatment.

The process is being operated in one steel mill as follows: The proper amount of pulverized limestone is added all at once from a weigh hopper to a batch of pickle liquor. The mixture is stirred until it turns light yellow, indicating that the ferric iron has been precipitated, and mixing is continued about ten minutes longer to expel the liberated carbon dioxide. Most pickle liquor contains enough ferric iron to produce this end point. Milk of lime is then run in until a red color is obtained with phenolphthalein indicator, and the treatment is completed by mixing for a few minutes longer. Phenolphthalein first gives a pink color with an alkali at a pH of about 8.3. From the time the test is taken until the lime feed is turned off, enough lime will normally have been added to raise the pH above 9; at this point complete precipitation of ferrous iron is insured.

Economy of operation can be effected by this process where the spent pickle contains a relatively high concentration of free acid, and where pulverized limestone is cheap compared with quicklime. In some localities pulverized limestone costs as much as quicklime on a basicity basis, and in that case the split treatment process would show no advantage. But the material can frequently be bought for 1 to 2 dollars a ton f.o.b., especially from quarries that do not operate lime plants.

Economic Factors in Neutralization¹⁵

The choice of the best neutralizing agent in any instance will be governed by the economic position of a given plant. Waste treatment practice varies so widely, because of the inherent complexity of the problems involved, that each installation must be designed to fit the particular situation of the plant for which it is intended. Pickle liquor neutralization plants also must be properly adapted to local conditions, and where there is a choice of alkaline agents it is important that the one best suited to the purpose be selected.

Two types of factors affect the choice of agent, (a) those fixed by the agent itself, such as basicity factor, delivered price, reactivity, etc.; and (b) those set by the conditions prevailing at a given mill, such as operating schedule, area available for the treatment plant, characteristics of the receiving stream or sewer system, and the like. Generally, the last-mentioned group of factors will be relatively unalterable, and an agent must be selected to meet those requirements. Only the cost of various agents will be mentioned here because that may constitute the principal operating expense.

Table 5 presents a listing of the relative costs of a number of common neutralizing agents. The prices in the fourth column are f.o.b. quotations as of February 1951. The fifth column lists basicity factors as units of calcium oxide equivalent per unit of sample; these factors were determined in the laboratory on representative commercial samples, except those for sodium hydroxide, sodium carbonate, and ammonia, which were calculated. The sixth column shows the cost of a ton of calcium oxide equivalent for each agent, and the seventh column the relative cost of each agent compared with high calcium quicklime.

TABLE 5. COST COMPARISON OF VARIOUS ALKALINE AGENTS

Agent	Grade	Container	Price, \$ ton in Car lots	Basicity Factor	Cost, \$/ton of Basicity	Rela- tive Cost
Sodium hydroxide	Flake (76%)	Drums	75.00	0.687	109.90	7.13
Sodium carbonate	Dense (58%)	Bags	32.00	0.507	63.11	4.10
Ammonia	Aqua (35%)	Drums	62.00*	1.647	37.61	2.44
Ammonia	Anhydrous	Tank Car	79.50	1.647	48.36	3.14
Magnesium oxide	Powder	Bags	75.00	1.306	57.43	3.73
High calcium hydrate	Chemical	Bags	14.50	0.710	20.45	1.33
Dolomitic hydrate	Chemical	Bags	16.50	0.912	20.13	1.31
High calcium quicklime	Pulverized	Bags	18.00	0.941	19.13	1.24
	Pulverized	Bulk	14.50	0.941	15.41	1.00
Dolomitic quicklime	Ground	Bags	15.50	1.110	13.94	0.90
	Ground	Bulk	12.00	1.110	10.79	0.70
High calcium limestone	Pulverized	Bags	5.00	0.489	10.23	0.66
	Pulverized	Bulk	3.50	0.489	7.15	0.46
Dolomitic limestone	Pulverized	Bags	5.00	0.564	8.86	0.57
	Pulverized	Bulk	3.50	0.564	6.21	0.40

*Price per ton NH_3 , as aqua ammonia.

It will be observed that Table 5 lists several alkaline materials that are quite costly as compared with high calcium lime. Sodium hydroxide would not be used for pickle liquor treatment unless recovery of iron oxide and sodium sulfate were contemplated; such a process would not usually be economically sound, but where there is a local market for sodium sulfate it might reduce the overall treatment cost. Sodium carbonate has been used where only the neutralization of free acid is required; it is useful for this purpose because it can be added dry, but, aside from its high price, it is an unsatisfactory agent for complete treatment because of its tendency to form soluble ferrous bicarbonate. A special procedure is necessary where ammonia can be used, and this is described later in the chapter; it would not normally be considered for neutralization on a small scale. Magnesium oxide is a rather costly compound that can be used where it is desired to recover iron oxide and magnesium sulfate; except under unusual

circumstances a process of this kind could be used only to reduce the net cost of treatment somewhat. When a pickle liquor neutralization plant is planned, neighboring industries should be surveyed to discover whether a suitable alkaline waste product is available. It happens occasionally that the wastes of two or more industries can be combined to effect a mutually advantageous solution for waste disposal.

BY-PRODUCT RECOVERY

The development of practical processes for recovery of useful products from spent pickle liquor has engaged the attention of a large number of workers, and their industry is evidenced by the eighty-odd processes that have been proposed. Unfortunately, few of these processes have ever been operated successfully on a commercial scale.

The various processes that have been proposed fall into a number of classes, as follows: recovery or manufacture of (a) copperas and lower hydrates of ferrous sulfate, (b) copperas and sulfuric acid, (c) ferrous sulfate monohydrate and sulfuric acid, (d) ferric sulfate and sulfuric acid, (f) electrolytic iron and sulfuric acid, (g) iron powder, (h) iron oxide for pigments or polishing rouge, (i) iron oxide and ammonium sulfate, and (j) constructional material. Hodge¹⁷ has described these processes in considerable detail, with an extensive bibliography. Only the more important processes are outlined here.

Copperas¹

Recovery of copperas from pickle liquor involves no unusual problems. Where recovery of the free acid is not desired, the waste liquor is heated with scrap iron to neutralize the acid, the resulting solution is settled to remove suspended matter, and the copperas is recovered as crystals, following either evaporation or refrigeration. By carefully drying the crystals, it is possible to produce lower hydrates, but ordinarily the drying is not carried beyond the trihydrate. Copperas-and-lime and chlorinated copperas are valuable coagulants for the treatment of water, sewage, and certain industrial wastes. Expansion of this market, especially near areas of steel production, is an attractive possibility.

Despite the simplicity of the recovery process, copperas manufacture cannot supply a satisfactory solution to the pickle liquor disposal problem, for a number of reasons. The demand for copperas in this country can be supplied by less than 4 per cent of the pickle liquor produced by the steel industry, and other enterprises, notably the manufacture of titanium dioxide, produce large quantities of this substance. Copperas cannot be shipped very far economically because 45 per cent of its weight is water of crystallization; this is an obstacle to the development of new markets.

The fact that ferrous sulfate and sulfuric acid are low cost chemicals demands that their salvage be accomplished by the simplest possible process and equipment. But hot, dilute sulfuric acid is very corrosive, and high equipment and maintenance costs are occasioned where it must be processed. Mills frequently have several pickling shops which are sometimes widely separated, and collection of the liquor for treatment in a single plant is always costly. Where production of more valuable derivatives is investigated, similar difficulties are met; moreover, no process would be practical which could be operated profitably by using waste acid and scrap iron as a starting point.

Copperas and Free Acid¹

Where the free acid is recovered for re-use, the makeup acid is usually added to the spent liquor prior to crystallization. This step reduces the solubility of ferrous sulfate and increases the efficiency of copperas recovery. In one process²⁸ the hot liquor is sprayed into the top of an open tower to take advantage of atmospheric evaporation. In another the liquor is concentrated in a vacuum evaporator until the sulfuric acid reaches a concentration of about 28 per cent²²; the liquor is then withdrawn, the copperas crystallized, and the acid returned to the picklers.

Ferrous Sulfate Monohydrate

The advantages of ferrous sulfate monohydrate (low water content, good storage properties, preferred form for sulfuric acid manufacture) have led to a number of processes for preparing this compound from pickle liquor. The principles used by the different processes are:

(a) Evaporation of the liquor, whose free acid has been neutralized with scrap, in a direct-fired rotary dryer.²⁷ (b) Evaporation of the neutralized liquor in a spray drier.²³ (c) Vacuum evaporation until the sulfuric acid concentration approaches 78 per cent, where ferrous sulfate is completely insoluble.²² (d) Autoclaving the liquor at 300° to 400°F and filtering the monohydrate without reducing temperature or pressure.²⁹ (e) Evaporation by submerged combustion.²⁴ (f) Continuous recirculation of the liquor through a direct-fired furnace, monohydrate removal equipment, and the pickling tanks.^{22A} The last four methods provide for recovery of the free acid. Several processes of this type have been used commercially.

Monohydrate produced by drying copperas is a mixture of hydrates usually containing about 1.5 molecules of water of crystallization. The product dissolves rather slowly in water, and this limits its usefulness. The salt which crystallizes from sulfuric acid, however, is a true monohydrate which dissolves rapidly.

Ferric Sulfate and Sulfuric Acid⁷

The autoxidation principle, which was patented in 1894, has attracted attention in recent years as a means for preparing ferric sulfate or sulfuric acid from spent pickle liquor. Although the proposed processes differ in some particulars, they depend upon the provision of intimate contact of air and sulfur dioxide with a solution of ferrous sulfate. It is claimed that this type of process can be controlled to produce either a strong solution of ferric sulfate or a 20 per cent solution of sulfuric acid. Such a process has been successfully operated in conjunction with a sewage treatment plant to provide ferric sulfate solution for use as a coagulant. If operating costs could be kept low enough, this type of process would find application in certain areas.

Iron Oxide and Sulfuric Acid⁸

One of the first rules of waste treatment practice is to attempt to convert a waste material into one or more other products which can be consumed in the establishment producing the waste. Conversion of spent pickle liquor into iron oxide and sulfuric acid would appear to fit this rule perfectly, and the problem of evolving a feasible process has been studied extensively. One process, which has operated successfully in another field, neutralizes the spent liquor with iron oxide and evaporates it to dryness in a direct-fired rotary kiln. The cinder is mixed with pyrite and roasted, and the purified kiln gas is converted to sulfuric acid in a vanadium contact plant. Other processes obtain sulfur dioxide by roasting a mixture of ferrous sulfate trihydrate with brown coal²⁶; dry copperas to the monohydrate and roast it in a Herreshoff furnace; spray-dry the neutralized liquor and roast the monohydrate in a special furnace to which a controlled amount of excess air is added to convert the sulfur dioxide to the trioxide through the catalytic effect of the hot, freshly formed iron oxide.

Manufacture of sulfuric acid from spent pickle liquor, by one means or another, is feasible, but such a method for utilizing the spent liquor has serious disadvantages. Sulfuric acid plants must be operated continuously and on a large scale (not less than 50 to 75 tons of acid per day) for reasons of economy. The installations are costly and maintenance charges high. Possibly no single mill produces enough pickle liquor to operate a plant of its own on a sound basis unless the cost of sulfuric acid increases markedly. Operation of a cooperative plant to serve a single steel-producing area has been discussed, but transportation and physical problems have interposed obstacles which appear to be insoluble. Alternatively, it has been suggested that monohydrate be produced at the mills and this compound be processed in existing acid plants for a conversion charge, but similar difficulties have prevented the development of a workable plan.

From the viewpoint of over-all economy, manufacture of sulfuric acid from pickle liquor is not especially attractive despite its apparent reasonableness, but exhaustion of supplies of natural sulfur may eventually alter the economics of acid manufacture.

Electrolytic Iron⁴

Several processes have been proposed for the recovery of iron from pickle liquor by electrolysis, but none has been notably successful. Ferrous iron tends to oxidize and precipitate basic salts; frequent regulation of the acidity of the bath is necessary to avoid this tendency and maintain a high cell efficiency. The cost of producing electrolytic iron requires a premium price for the product; production of silicoirons and alloys with low hysteresis losses have discouraged the development of electrolytic iron installations.

Iron Powder

The increasing utility of various metal powders for use in the operations of powder metallurgy has drawn the attention of several investigators to the iron oxide obtainable from pickle liquor as a raw material for reduction. It has been predicted that the market for iron powder could be extended considerably if a product of proper quality could be produced at a price appreciably below the current market. Preparation of the oxide in suitable form for reduction, and sources of cheap hydrogen have been obstacles to the development of a sound process.

Iron Oxide Pigments⁸

Various natural iron oxides have been used as pigments since ancient times, and similar products are manufactured by decomposing copperas under controlled conditions. No special problems are involved where the pigments are produced by those skilled in the art, but the consumption of these products is relatively small in comparison with the total amount of spent pickle liquor available.

Construction Material²⁴

Ferron, a constructional material with interesting possibilities, has been made from the sludge which results when pickle liquor is neutralized with lime. The plastic material so produced is blended with fillers in a pug mill, pressed into sheets or blocks, and dried at 175°F. A plasterboard has been made whose physical performance is reported to equal that of products made from gypsum. Shingles have been made by incorporating an asphalt emulsion with the sludge, and performance tests indicate that they are of good quality. This kind of product probably could not be

manufactured at a cost competitive with natural gypsum materials, but it might be used to reduce treatment costs.

Ammonium Sulfate⁵

The obviousness of combining spent pickle liquor with coke oven ammonia to produce ammonium sulfate and iron oxide has encouraged many research workers to investigate the practicability of such a procedure. The obstacles to the development of a feasible process were very great, e.g., difficulty of eliminating impurities in ammonia and pickle liquors to avoid contamination of the ammonium sulfate, separation of the hydrated iron oxides from the sulfate liquor, evaporation of large volumes of water, and lack of stoichiometric relations between pickle liquor and ammonia. Nevertheless, a number of processes were developed, some industrially; but none ever reached successful commercial operation, largely because of the costly equipment required, corrosion encountered and difficulty in producing an acceptable ammonium sulfate.

MELLON INSTITUTE RESEARCH

The steel industry has long recognized its public responsibility to abate stream pollution arising from its widespread operations. Individual companies have conducted independent research on pickle liquor treatment for many years, and several costly installations were made which proved to be economically impractical.

The size and complexity of the pickle liquor problem convinced the American Iron and Steel Institute that optimum progress could be made if a separate organization were authorized to study it on an industry-wide basis. This decision was implemented in 1938 by sponsorship of a research program at Mellon Institute. The purpose of this project was to correlate the efforts of individual companies and to conduct original research in an atmosphere free from the interruptions which frequently interfere with this type of work in steel mills. This project led to the development of a number of processes that appear to have some economic potentiality. These processes, which will be briefly described, have been studied only on a small scale. Pilot plant investigations would be essential to sound economic evaluation in every case.

Iron Sulfates in Cement¹⁸

The setting time of Portland cement is regulated by grinding 2 to 3 per cent of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, with the cement clinker. Laboratory investigation has indicated that iron sulfate, on an SO_3 basis, can be substituted for gypsum. Experimental cements containing iron sulfate

compared favorably with commercial Portland cements in setting time and in tensile and compressive strengths. Test briquets made from samples of the experimental cements which had been stored for 5 years showed no appreciable diminution in strength. If this use for ferrous sulfate were adopted generally, it would consume more of the compound than is produced as spent pickle liquor.

There are, unfortunately, a number of serious drawbacks to this apparently simple method of utilizing pickle liquor. The procedure has not been studied on a commercial scale, and, until this is done, there is no guarantee that the laboratory results can be duplicated in practice. Although the pale brown color of cement containing iron sulfate would be desirable for highway construction to reduce glare, contractors and consumers would have to be converted to the use of the new material. Amendment of the specifications of the American Society for Testing Materials would be necessary before the substitution would be permitted. The most significant objection, however, is the improbability that sulfate as copperas could be purchased at as low a price as sulfate in the form of gypsum.

Differential Solubility¹⁰

Certain water-soluble organic solvents have the property of reducing the solubility of moderately soluble inorganic salts. This principle was applied to spent pickle liquor, and a large number of solvents was investigated. Acetone was finally determined to be the most generally satisfactory agent for the purpose, and a practicable process was devised.

The unit operations involved are rather simple in themselves. Equal volumes of acetone and pickle liquor are mixed thoroughly; the finely crystalline copperas is separated in a basket centrifuge; and the acetone is recovered from the mother liquor by fractionation. Practically all of the free acid is recovered in the still bottoms which, when made up to pickling strength with fresh acid, will contain less than 2 per cent of ferrous sulfate.

A laboratory study of the free acid recovered in this process indicates that it is suitable for re-use in the picklers. Six pickling and recovery cycles were made in which the operations of batch pickling were simulated, and there was no tendency for impurities to accumulate in the liquor. The recovered acid appeared to be the equivalent of fresh acid as a pickling agent.

This process has the advantage of recovering 95 per cent of the ferrous sulfate and substantially all of the free acid in waste pickle liquor. The recovered acid solution contains a lower proportion of ferrous sulfate than similar solutions from refrigeration processes. On the other hand, the process depends upon a relatively expensive, highly flammable solvent of which not less than 99.5 per cent must be recycled.

Ferrie Chloride and Sodium Sulfate

The desirability of converting the iron in spent pickle liquor into compounds more valuable than copperas led to the development of a feasible process for producing saturated ferrie chloride solution and pure anhydrous sodium sulfate. Where the spent liquor is treated with an excess of sodium chloride, a double salt of iron and sodium sulfate precipitates. Glauber salt, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, is separated from the mixture by successive crystallizations, and during these operations a ferrous chloride solution is produced from which a small amount of residual sulfate is precipitated by addition of calcium chloride. The ferrous chloride solution is chlorinated and evaporated to a 60 per cent solution of ferrie chloride. At this concentration practically all of the excess sodium chloride precipitates; it is filtered off and returned to the process. At 60°C Glauber salt melts in its water of crystallization and precipitates anhydrous sodium sulfate. The sodium sulfate is filtered off and the mother liquor recycled.

This is a practicable process for producing a saturated solution (60 per cent) of ferrie chloride, and anhydrous sodium sulfate containing not more than 0.05 per cent of iron and 0.15 per cent of sodium chloride. The process has the disadvantage of requiring a number of filtrations and refrigerations which must be carefully controlled for best results. The demand for pure sodium sulfate and the increasing usefulness of ferrie chloride may, in time, improve the commercial potentiality of the process.

Manganese Concentrate¹¹

This country has large deposits of low grade manganese ores but almost none of sufficiently high grade for conversion to ferromanganese, an essential product required for manufacturing steel. The shortage of manganese was acute in the early days of World War II, and an investigation was made to determine whether the reducing property of ferrous sulfate could be employed to concentrate the manganese in low quality pyrolusite ores.

Low grade ore is ground to —60 mesh, mixed with a small excess of pickle liquor, and the gangue separated by filtration. The clear extract consists of manganous and ferrie sulfates, plus a small amount of ferrous sulfate. The sulfates are converted to chlorides by treatment with calcium chloride, and the gypsum which precipitates can be recovered as a compound of high purity. The ferrie iron in the filtrate is precipitated by controlled treatment with precipitated chalk. The filtrate is treated with lime slurry to precipitate the manganese, which is filtered off, washed, and dried as the main product. The filtrate from this step is substantially a solution of calcium chloride; it is reduced by evaporation and returned to the process.

This process produces a manganese concentrate containing upwards of

60 per cent manganese and two by-products of low value. Its principal disadvantage is one of geography; most of the suitable manganese ores are mined at a great distance from the centers of steel manufacture.

Current research on this process indicates that a solution of ferrous sulfate containing no free acid can be used to extract the manganese and that the technology involved can be simplified. These developments should improve the economy of the process and increase its usefulness.

Magnesia

The economical recovery of magnesia from dolomite is a problem which has attracted considerable attention. The advantage of being able to use a waste product to effect such a recovery suggested that pickle liquor might be suitable for the purpose, and a rather simple process was evolved.

The sulfates in pickle liquor are converted to chlorides by treatment with calcium chloride, and pure gypsum is filtered off. The iron is precipitated by controlled treatment with dolomitic lime slurry, and the precipitate is discarded. More dolomitic lime is then added to the filtrate to precipitate the magnesia, and the calcium chloride brine remaining is evaporated and recycled.

In the laboratory, magnesia of 91 to 94 per cent purity was prepared by this process. The chief contaminant of the magnesia was calcium oxide, and this compound could be leached with water to improve the quality of the principal product. The hydrated iron oxide which is precipitated in the iron removal step has a high sulfur content that cannot be reduced without impairing the quality of the magnesia. Evaporation of the large volume of wash water required for recovery of calcium chloride is a disadvantage.

Ammonium Sulfate¹⁰

The obstacles to the development of a sound process for combining coke oven ammonia and spent pickle liquor have been considerable, but the advantages of a feasible process of this kind could be very great. After a lengthy study of the factors involved, a process was developed which appears to have overcome the chief difficulties which were encountered by prior workers.

Purified ammonia and pickle liquor are fed continuously to a reactor of special design in which the precipitated ferrous hydroxide is oxidized under carefully controlled conditions to ferrous-ferriic oxide; by this means the iron is precipitated completely. The magnetic iron oxide produced in this manner settles rapidly (95 per cent in 5 minutes), and it can be separated from the ammonium sulfate liquor by continuous decantation. Separation of the iron oxide was the operation which defeated many of the

previous processes. Pure ammonium sulfate is recovered by evaporation of the final clear liquor.

Based upon small scale pilot plant studies, the economics of the process appear to be sound. The obvious economic advantage of the process is the ability to substitute the sulfate in the pickle liquor for the sulfuric acid used in the ammonia saturators to manufacture ammonium sulfate.

A process based on direct treatment of coke oven ammonia with pickle liquor would have several obvious advantages, and such a process was developed, using the principles outlined for pure ammonia. Preliminary studies were made with coke oven ammonia liquor, fortified with additional sulfides and cyanides, to determine the maximum limits of impurities for production of pure ammonium sulfate. The process was later operated with pickle liquor that had been used to scrub ammonia, sulfides and cyanides from coke oven gas. Ammonia can be removed completely from the gas, and hydrogen sulfide is removed in proportion to the ferrous iron in the pickle liquor. Oxidation of the iron in this liquor is carried to ferric oxide to produce a settleable and filterable material. This step also causes the sulfur that had been combined with the iron to separate as elemental sulfur which can be recovered by flotation or by solvent extraction. The cyanides are removed in combination with the iron oxide sludge.

This process not only saves the sulfuric acid now used in the ammonia saturators, but it reduces the sulfur in the coke oven gas, thereby making it a more desirable fuel for many steel mill purposes. It has been demonstrated that pure ammonium sulfate can be prepared from gas containing a considerably higher concentration of sulfide and cyanides than is normally present. The cyanides can be completely recovered from the sludge by extraction with caustic soda.

The process would appear to offer an advantageous method for disposing of pickle liquor and accomplishing other desirable results. There are, however, a number of technical problems that decrease its attractiveness. Pickle liquor and coke oven ammonia are rarely in stoichiometric balance; usually there is a substantial deficiency of the former. This means that existing ammonia saturators would have to be retained to remove the surplus ammonia. Where pickle liquor and ammonia are in balance, the liquor will usually contain only enough iron to combine with about half the hydrogen sulfide in the gas. In such cases, supplemental sulfide removal equipment would have to be operated where a low concentration in the gas is essential. Coke ovens and pickling shops are not often close enough to each other to avoid costly pickle liquor transport equipment. For sound economic evaluation the process would have to be operated on a pilot scale at a steel mill, and this has not yet been done. It is possible that the

process will eventually prove to be economically feasible, but further plant-scale investigation will first be necessary.

Ferric Sulfate

A process has been evolved whereby pickle liquor can be oxidized to a solution of ferric sulfate. The process employs the autoxidation principle and involves dispersion of a stream of sulfur dioxide and oxygen in pickle liquor at 60°C. The gases are dispersed by an impeller of special design that causes a shearing action and thus distributes the gases as thin films. The process yields ferric sulfate up to a concentration of 150 grams per liter with a low free acid content. Such a process could be applied in areas where a source of waste sulfur dioxide is available. The resultant solution could be concentrated by evaporation, if desired, for shipment to relatively nearby points of consumption, or it might be spray-dried to yield the anhydrous salt.

Stainless Steel Pickle Liquor

The research program has been almost completely occupied with investigations of sulfate liquors, but attention has been given to treatment of spent liquor from stainless steel pickling. These liquors usually contain the salts of iron, chromium, and nickel in an aqueous solution of nitric and hydrofluoric acids. The relatively high value of the compounds dissolved in such liquors favors the economic practicability of a recovery process. Preliminary study has shown that pure calcium nitrate and a sludge of metal oxides can be obtained by treatment of the liquor with high calcium lime. The nitrate finds a good market in the fertilizer field, and the oxides can be sintered for recharging to the furnaces. Separation of the sludge from the calcium nitrate liquor is rather difficult, but centrifugation offers a reasonably satisfactory means for the purpose.

Stainless steels are made in the electric furnace. Since the blast furnace provides a less costly method for reducing iron oxide to the metal there would be an advantage in recovering the chromium and nickel separate from the iron in stainless steel pickle liquor. Experiments demonstrated that only about 40 per cent of the iron can be differentially precipitated from such liquor without losing a considerable proportion of the chromium.

Acknowledgment

The publications of the American Iron and Steel Institute Fellowship at Mellon Institute have been drawn upon extensively in the preparation of this chapter. The reader should refer to these papers for more detailed information on specific points.

References

1. Agde, G., *Stahl u. Eisen*, **57**, 789-93 (1937); Droof, J., *Ibid.*, **57**, 838-9 (1937); Marsh, H. S., and Cochran, R. S., U.S. Patents, Reissue 15,119 of 1,369,451 (1921), 1,450,216 (1923), and 1,589,610 (1926); Zahn & Co., G.m.b.H., French Patents 723,484 (1931) and 808,033 (1937).
2. American Iron and Steel Institute, Annual Statistical Rept., 1949.
- 2a. Bartholomew, F. J., *Chem. Eng.*, **57**, 118-20 (1950).
3. Coleman, H. S., and Coleman, F. H., U.S. Patent 2,063,029 (1936).
4. Creighton, H. J., and Koehler, W. A., "Principles and Applications of Electrochemistry," Vol. 2, 232. New York, John Wiley & Sons, 1944.
5. Davies, D., Jr., U.S. Patent 1,942,050 (1934); Falding, F. J., *Ibid.*, 961,763-4 (1910); Falding, F. J., and Cathcart, W. R., Brit. Patent 11,364 (1910); Harris, A. W., U.S. Patent 1,994,702 (1935); Sierp, F., *Stohl u. Eisen*, **58**, 491-7 (1938); Sperr, F. W., Jr., U.S. Patents 1,928,510 (1930), 1,983,320 (1934), and 1,986,900 (1935).
6. Diescher, S. E., *Ibid.*, 1,023,458 (1912).
7. Emmens, S. H., *Ibid.*, 513,490 (1894) and 543,002 (1895); Keyes, H. E., *U.S. Bur. Mines, Bull.*, 321 (1930); Lyles, J. E., *J. Am. Water Works Assoc.*, **26**, 1214-18 (1938).
8. Fireman, P., U.S. Patent 1,287,939 (1918); Kaplan, B. B., *Proc. W. Vo. Acad. Sci.*, **4**, 90-2 (1930); *Ibid.*, U.S. Patent 1,878,525 (1932); Parker, T., British Patent 24,859 (1895); Reavell, J. A., *J. Soc. Chem. Ind.*, **47**, 347-51T (1928); Sierp, F., *Stohl u. Eisen*, **58**, 491-7 (1938).
9. Gehm, H. W., *Chem. Met. Eng.*, **51**, 124 (Oct. 1944).
10. Hoak, R. D., U.S. Patent 2,529,874.
11. Hoak, R. D., U.S. Patent 2,462,499; Hoak, R. D., and Coull, J., *Chem. Eng. Prog.*, **46**, 158-62 (1950).
12. Hoak, R. D., Lewis, C. J., and Hodge, W. W., *Ind. Eng. Chem.*, **36**, 274-8 (1944).
13. *Ibid.*, **37**, 553-59 (1945).
14. Hoak, R. D., Lewis, C. J., Sindlinger, C. J., and Klein, B., *Ibid.*, **39**, 131-35 (1947).
15. *Ibid.*, **40**, 2062-67 (1948).
16. Hoak, R. D., and Sindlinger, C. J., *Ibid.*, **41**, 65-70 (1949).
17. Hodge, W. W., *Ibid.*, **31**, 1364-81 (1939).
18. Hodge, W. W., U.S. Patent 2,307,270 (1943).
19. *Ibid.*, 2,322,134 (1943).
20. Jones, E. M., *Sewage & Ind. Wastes*, **22**, 224-27 (1950).
21. Lewis, C. J., *Iron Age*, **163**, No. 3, 48-53 (Jan. 20, 1949).
22. Mantius, Otto, *Wire and Wire Products*, **13**, 585-9 (1938).
- 22a. Martin, E. D., *Blast Furnace Steel Plant*, **36**, 1089-94 (1918).
23. Reavell, J. A., *J. Soc. Chem. Ind.*, **47**, 347-51T (1928).
24. Rentschler, M. J., *Iron Steel Engr.*, **16**, 52-62 (1939).
25. Rosenstein, L., U.S. Patent 2,055,419 (1936).
26. Sierp, F., *Stohl u. Eisen*, **58**, 491-7 (1938).
27. Spangler, S. F., *Blast Furnace Steel Plant*, **23**, 319-21 (1935); *Chem. Met. Eng.*, **42**, 139-41 (1935); Spangler, S. F., and Titlestad, N., *Wire and Wire Products*, **13**, 591-4 (1938).
28. Stevenson, E. P., U.S. Patent 1,515,799 (1924).
29. Whetzel, J. C., and Zimmerman, R. E., *Ibid.*, 2,005, 120 (1935).
30. Wing, W. E., *Proc. 5th Ind. Waste Conf.*, Purdue U., Series No. 72 (1949).

13. Plating Wastes

M. Gilbert Burford and Joseph W. Masselli

*Wesleyan University and The Connecticut State Water
Commission Laboratory, Middletown, Conn.*

Although wastes from the plating industry do not approach the volume of wastes produced by some other industries, they are nevertheless important sources of pollution because of the extremely toxic nature of the constituents. These constituents are mainly inorganic in nature, the most important ones being acids, metals such as copper, zinc, nickel, cadmium and chromium, and the highly dangerous cyanides. In general the tolerable limits of such wastes are considerably lower than with the organic type of pollution, but, fortunately, good methods of treating the wastes are generally available.

PLATING ROOM PROCESSES

For convenience, plating room processes which contribute to polluting wastes may be separated into the three headings of stripping, cleaning and plating.

Stripping

Stripping processes are necessary for the removal of undesirable metallic, metallic oxide, or other coatings which may be on the work to be plated. The type of stripping process will depend on the film to be removed and the base metal involved. Most stripping baths are acidic in nature and usually consist of solutions of sulfuric, nitric, hydrochloric and hydrofluoric acids, the latter being used less frequently. The plating literature lists special stripping baths involving the above acids and many other chemicals,³⁰ but the other chemicals are present in low concentrations and will not generally modify the total effluent picture. In addition to the acidic baths, alkaline baths with sodium sulfide, sodium cyanide, sodium hydroxide and sulfur may also be used. The range of concentrations of individual chemicals in the stripping baths is usually 5 to 10 per cent. During recent years the electrolytic method of stripping has been

increasingly used because of its rapid action. In this method the material to be plated is made the anode, usually in baths equivalent to those mentioned above. The end products in both processes are essentially the same.

Cleaning

Cleaning processes are mainly designed to remove soil, oil and grease. They are usually of three general types: organic solvent vapor cleaners, acid pickling cleaners and alkaline cleaners. Organic solvent vapor cleaners are used mainly for oil and grease removal. They do not contribute significantly to the industrial waste. Acid pickling cleaners are used mainly for the neutralization of alkaline cleaners previously used in the cleaning process and for surface preparation. They generally consist of sulfuric, hydrochloric or nitric acid, usually in 1 to 5 per cent concentrations.

Alkaline cleaners consist of organic emulsion cleaners, alkali soaking cleaners, and alkali electro-cleaners. The organic emulsion cleaners are petroleum or coal-tar solvents coupled with an emulsifier. They are used both diluted and undiluted for soak cleaning and are usually followed by an alkali cleaner. Alkali soaking cleaners are commonly used at 4 to 16 ounces per gallon concentrations. They consist of sodium hydroxide, ortho-phosphates, complex phosphates, silicates, carbonates, potassium hydroxide, organic emulsifiers and synthetic wetting agents.

Alkali electro-cleaners are similar to soaking cleaners with two exceptions. They usually do not contain organic emulsifiers or synthetic wetting agents, and the alkalinity balance is different so as to give greater conductance. They can be used as either anodic or cathodic electro-cleaners. Cathodic cleaning is usually followed by anodic cleaning, often merely by reversing the polarity on the material in the same bath.

Plating

In the plating process the actual deposition of the metal takes place. The material being plated is made the cathode in an electrolytic cell. Typical compositions of some of the more common plating baths are listed in Table 1. Significant metal and cyanide concentrations are recorded along with concentrations to be expected in a 4 gallon per minute (gpm) rinse, assuming "drag-outs" of 0.5 and 2.5 gallons per hour (gph).*

Many other metals such as gold, platinum, rhodium, and palladium are also used for plating, and formulas for these baths may be found in the literature.³⁹ However, careful precautions are taken in the industry to avoid losing these expensive metals and they do not ordinarily present a pollution problem except insofar as the disposal of cyanide is concerned

TABLE 1. COMMON PLATING BATHS

Bath Formulas	Metallic + Cyanide Concentrations in ppm	Rinse Concentration in ppm 0.5 gph Drag-out	Rinse Concentration in ppm 2.5 gph Drag-out
Nickel			
40 oz/gal nickel sulfate	82,000 Ni	171 Ni	855 Ni
8 oz/gal nickel chloride			
6 oz/gal boric acid			
Chromium			
53 oz/gal chromic acid	207,000 Cr	431 Cr	2,155 Cr
0.53 oz/gal Sulfuric acid			
Copper (acid)			
27 oz/gal copper sulfate	51,500 Cu	107 Cu	535 Cu
6.5 oz/gal sulfuric acid			
Copper (cyanide)			
3.0 oz/gal copper cyanide	12,400 Cu	2.8 Cu	14 Cu
4.5 oz/gal sodium cyanide	28,000 CN	58 CN	290 CN
2.0 oz/gal sodium carbonate			
Copper (pyrophosphate)			
4 oz/gal copper (as proprietary mix)	30,000 Cu	62 Cu	310 Cu
29 oz/gal sodium pyrophosphate			
0.1% ammonia (by volume)			
Cadmium			
3.5 oz/gal cadmium oxide	23,000 Cd	48 Cd	240 Cd
14.5 oz/gal sodium cyanide	57,700 CN	120 CN	600 CN
Zinc			
8 oz/gal zinc cyanide	33,800 Zn	70 Zn	350 Zn
5.6 oz/gal sodium cyanide	48,900 CN	102 CN	510 CN
10 oz/gal sodium hydroxide			
Brass			
4 oz/gal copper cyanide	21,000 Cu	41 Cu	220 Cu
1.25 oz/gal zinc cyanide	5,250 Zn	11 Zn	55 Zn
7.5 oz/gal sodium cyanide	47,500 CN	99 CN	495 CN
4 oz/gal sodium carbonate			
Tin (alkaline)			
16 oz/gal sodium stannate	53,000 Sn	110 Sn	550 Sn
1 oz/gal sodium hydroxide			
2 oz/gal sodium acetate			
Silver (cyanide)			
4 oz/gal silver cyanide	21,600 Ag	51 Ag	255 Ag
4 oz/gal sodium cyanide	21,800 CN	45 CN	225 CN
6 oz/gal sodium carbonate			

*"Drag-out" is the amount of solution carried out of the bath by the material being plated and the racks holding the material.

Rinse rate is assumed to be 4 gpm

Flow sheets for typical conveyORIZED plating machines are shown in Figure 1. In addition to the process baths outlined there, a stripping bath and possibly a pre-cleaning bath may also be used. ConveyORIZED systems

Copper Plating		Nickel Plating		Chrome Plating		Zinc Plating	
Electrocleaner (Cathodic)		Electrocleaner (Cathodic)		Electrocleaner (Cathodic)		Electrocleaner (Cathodic)	
Running Rinse	→	Electrocleaner (Anodic)		Running Rinse	→	Running Rinse	→
Hydrochloric Acid Dip (5%)		Running Rinse	→	Sulfuric Acid Dip		5% Sulfuric Acid Dip	
Running Rinse	→	5% Sulfuric Acid Dip		Running Rinse + spray	→	Running Rinse	→
Copper Cyanide "Strike"		Running Rinse	→	Chrome Solution		Zinc Cyanide Solution	
Running Rinse	→	Bright Nickel Solution		Recovery Rinse		Running Rinse	→
Running Rinse	→	Running Rinse	→	Mist Spray Rinse		Spray Rinse	→
Copper Pyrophos- phate Solution		Soap Dip		Running Rinse	→	Brightener Still Dip (HNO ₃)	
Running Rinse	→	Hot Running Rinse	→	Hot Still Dip		Running Rinse	→
Hot Rinse (Slow overflow)	→	Drying Oven		Running Rinse	→	Running Rinse	→
Drying Oven				Hot Rinse (Slow overflow)	→	Hot Water Dip (Slow overflow)	→
				Drying Oven		Drying Oven	

FIGURE 1. Flow sheets for common types of conveyORIZED electroplating.
(Wastes overflowing to final effluent are indicated by an arrow)

usually have a maximum number of rinses because of the progressive movement of the material being plated. In manual plants one rinse bath may be used for rinsing the work from several different solutions. The solution volumes commonly range from 50 gallons up to several thousand

gallons and the rinses are contained in steel tanks with noncorrosive linings. All wastes which overflow into the final effluent are indicated by an arrow.

SOURCES OF WASTES

The main sources of waste in electroplating plants are drag-out losses carried into overflow rinses, spray loss, solution dumping, and leakage. Drag-out losses vary considerably, depending on the bath concentration and temperature, the shape of the material being plated, the position of the material on the racks, the time allowed for drainage, the drain holes in the articles, the extent of the recovery system and the efficiency of its operation, the coating on the rack fixtures, and the number of pieces being plated. Drag-out volumes in a fully-loaded conveyorized plant, plating approximately one million pieces of 0.1 to 3 square feet area per week, have been observed to vary between 1 and 4 gallons of bath solution per hour, with most values lying between 1.5 and 2.5 gph. Manual plants will generally show larger drag-out losses than comparable automatic plants. These drag-out solutions are immediately diluted by the overflow rinse volumes, which have been observed to vary from 1 to 8 gpm (probable average about 4 gpm). Such dilution is considerable, as can be noted from the rinse concentrations which have been calculated for 0.5 gph and 2.5 gph drag-outs into a 4 gpm rinse (see Table 1). The figure of 0.5 gph is taken as an average for a plant plating small objects, and 2.5 gph as an average for plants plating larger material. Larger average drag-outs are usually avoided by allowing longer periods for drainage.

Spray loss of plating solution occurs mainly with chrome plating since vigorous gas evolution accompanies this process. An exhaust system is usually installed to recover the finely divided spray produced by these gases. This is composed of slots in the sides of the tanks above the level of the liquid, leading into channels which are ventilated by an exhaust fan. The spray usually passes through a solution recovery chamber and is periodically returned to the tank. The efficiency of the recovery will depend on the distance between the solution level and the draft slots.

Dumping of spent, spoiled, or obsolete solutions is commonly practiced with stripping and cleaning solutions only. This may be done as often as once a week. There is considerable variation in the dumping of metallic plating baths. In general most plants dump such baths only after remedial measures fail to restore them and this may occur only after years of use. Some plants interested in fine finishes, however, are reported to dump baths once a week, and a few plants will dump baths rather than take the trouble to restore them.

Under no condition should any bath ever be dumped directly to a sewer or stream, because of the highly toxic and corrosive nature of the compounds present. The seriousness of such a matter may be indicated by the fact that a 100-gallon tank of a 50,000 ppm cyanide solution, even though diluted by 50,000,000 gallons of water, would provide enough cyanide to be toxic to fish. One hundred gallons of chromium plating solution, even though diluted by 200,000,000 gallons of stream water, would provide enough chromate to kill most of the fish-food present. If dumping is necessary, this should be done directly to a treatment tank or to a protected lagoon and the strong solution should be proportioned into the weaker wastes.

Leakage of plating solution is perhaps not common but instances of slow leaks which have gone undetected for a considerable period of time have been noted. These seriously increase the toxic nature of the waste.

CHARACTER AND STRENGTH OF WASTES

The character and strength of plating wastes vary considerably, but certain general characteristics may be pointed out. The wastes will usually consist of low concentrations of such metals as copper, nickel, zinc, cadmium, chromium, and tin in solution, either as the simple ions or as cyanide complexes. Excess sodium or potassium cyanides will also usually be present. In addition to these, some concentration of iron or other metal ion will be obtained from the base metal by solution in the stripping and cleaning processes.

An idea of the relative concentrations of the metals involved may be obtained by inspection of the concentrations recorded in Table 1. For example, the chromium concentration in the chrome bath is 2.5 to 18 times the metal concentrations in the other baths. The nickel concentration in its bath is also fairly high, and thus these two may be expected to be found in relatively higher concentrations. The copper, zinc and cadmium ion concentrations are generally lower than nickel and chromium, and the cyanide content may be expected to be intermediate between these and the nickel concentration. This order of concentration may be expected to be found in plants where the machines plate approximately the same amount of materials.

Although the rinse concentrations listed in Table 1 indicate only the concentrations expected to be found in the rinses immediately following the baths, they may be used to calculate roughly the order of concentration to be expected in the final mixed effluent. This may be done by counting the number of rinses in the plant and diving into the concentration range listed (all rinse rates are assumed to be equal). For example, a plant containing the four machines designated in Figure 1 would have

22 rinses and each rinse would therefore be diluted 22 times. Assuming a 4 gpm rate in all rinses and a 2.5 gph drag-out from each plating bath, the following concentrations would be expected in the final mixed effluent: 100 ppm chromium, 40 ppm nickel, 14 ppm copper, 11 ppm cadmium, 16 ppm zinc, and 50 ppm cyanide. The same processes in a manual plant would probably have only eleven rinses and the concentration would thus be about double those reported above.

These theoretical calculations are presented merely as an example of a procedure which has been helpful in surveying a given plant. For any actual case it would obviously be necessary to obtain chemical analyses of the various baths and as accurate figures as possible on the drag-out and rinse rates to make the calculations of any significance. In addition, of course, there would have to be complete chemical analyses of the over-all wastes actually produced. However, if there are serious discrepancies between the calculated and observed figures, this is an indication of additional sources of waste or leakage, or perhaps of interaction of the wastes before they reach the collection points. Such information may often prove of great value.

TABLE 2. PLATING WASTE CONCENTRATIONS

Plant	pH	Copper	Iron	Nickel	Zinc	Chromium		Cyanide
						Cr ⁶⁺	Total	
A	3.2	16	11	0	0	0	1.0	6
	10.4	19	3	0	0	0	0.5	14
B	4.1	58	1.2	0	0	204	246	0.2
C	2.8	11	—	0.2	—	3	7	1.2
D	2.0	300	10	0	82	0	0	0.7
E	2.4	35	8	—	—	555	612	1.2
	10.7	14	4	19	—	32	39	2.0
F	10.5	6	2	25	39	—	—	10
G	11.3	18	18	26	—	36	—	15
	11.9	23	21	32	—	95	—	13

(All analyses, except pH, are expressed in parts per million (ppm).)

The over-all waste may be either acidic or alkaline, depending on the type of baths used. A preponderance of cyanide or alkaline cleaning baths with their high associated alkalinity is likely to produce a highly alkaline reaction, but the presence of a chromate bath with its high acidity may produce a highly acid reaction. The extent of activity in the stripping room is an important factor in fixing the final pH because of the high acidities of the solutions usually used there.

Chemical analyses of over-all wastes from some typical plating plants are recorded in Table 2. It will be noticed that the cyanide concentrations listed here are lower than those which would be obtained by the method

of calculation outlined above. However in these cases it is known that local acidification of the cyanide wastes may occur, with consequent evolution of hydrogen cyanide before the wastes reach the collection points. Some cyanide may also be removed by precipitation.

The total volume of wastes from different plating plants will vary tremendously. In Connecticut the range is from 2,000 to 350,000 gallons per day.

REMEDIAL MEASURES

The pollution power of plating wastes may be reduced within the plant by several means. The most fruitful source of reduction is usually through drag-out minimization. Drag-out may be reduced by properly designing and racking for quick drainage, by allowing greater time for drainage, and by the use of smooth rack coatings without porous nodules or air holes. The use of stationary recovery rinses following each plating solution has also been found to be effective in drag-out reduction.³⁷ Two such rinses in succession will result in very low drag-out losses. When the first recovery rinse water becomes fairly high in concentration, the contents of the tank may be emptied into the plating bath or a storage tank for use as make-up water. The rinse tank may then be filled with the solution in the second recovery rinse, which is again filled with tap water. In this way very little drag-out reaches the final plant effluent.

Spray loss is another source where reduction may be effected, usually by the means previously indicated.

Reduction in water consumption will also reduce pollution power, in addition to lowering plating costs, since the metallic compounds precipitated in the treatment methods are soluble to an absolute extent dependent on the total volume of waste water. In addition, an increase in the usual metallic concentrations found in plating wastes generally increases treatment efficiency. One method of reducing water consumption is to use series rinses in place of parallel rinses wherever possible. For example, the second overflow rinse after the chromium recovery rinse may be reused as rinse water after the zinc plating bath. Total water consumption may be reduced 10 to 40 per cent in conveyORIZED machines by this method. The possibility of the use of lower rinse rates should not be overlooked, since rates higher than those needed for adequate rinsing have been noticed in many plants.

Another obvious means of reducing pollution load is by the exercise of adequate chemical control over the plating baths so that dumping is less frequently necessary.

EFFECT OF WASTES

An excellent critical review of the general literature on toxic material

has been compiled by Rudolfs, *et al.*⁷² Only the substances of particular importance in electroplating wastes are discussed here.

The effect of electroplating wastes may be conveniently divided into three fields:

- (1) Toxicity to fish and fish food.
- (2) Effect on sewers.
- (3) Effect on sewage treatment processes.

Toxicity to Fish and Fish Food

The toxic effects on fish and fish food of some of the chemicals which may be found in plating wastes are listed in Table 3. These values indicate the extreme toxicity of electroplating compounds, and may be used to measure the efficacy of a given treatment method. There are many difficulties in the exact determination of the limits of toxicity of any substance, however, and because of this the recorded values should be used only as conservative guides. Some of the variables which have been found to have a significant effect on toxicity are the size, age, hardness, and species of the fish or fish food used as the test organism. The pH, the temperature, the hardness, the total alkalinity, the oxygen content, and the other dissolved substances in the receiving water are also of importance. In addition, the type and amount of stream biota, the degree and nature of other pollution sources, the extent of stratification, the amount of aeration, and the presence of synergistic or antagonistic compounds in the water must also be taken into account.^{8,24}

Since these toxicity tests have been based on relatively short-time effects only, no information concerning the cumulative effects of concentrations below those recorded is indicated. Such cumulative effects are believed to be important, and because of this the values listed may be taken as conservative.

Effect on Sewers

The acidic wastes produced in electroplating processes are corrosive, and will thus attack metal and concrete structures.⁷³ In addition, acids convert the soaps in sewage to fatty acids, forming floating scum which clings to objects and which leads to sludge-dewatering difficulties because of the production of a sticky sludge.⁸⁸

Alkaline wastes from the plating plant are also corrosive but this type is generally not as aggressive as that caused by acid wastes.

Effect on Sewage Treatment Processes

Plating wastes have a deleterious effect on sewage treatment processes because of the toxic reaction of the waste chemicals on the biological

TABLE 3. TOXICITY TO FISH AND FISH FOOD

Substance	Concentration		Test Organism	Effect	Ref.
	ppm	As			
Chromic acid	0.3	Cr	<i>Daphnia magna</i> *	Toxic	4
Hydrochloric acid	62	HCl	<i>Daphnia magna</i> *	Toxic	4
Nitric acid	107	HNO ₃	<i>Daphnia magna</i> *	Toxic	4
Sulfuric acid	88	H ₂ SO ₄	<i>Daphnia magna</i> *	Toxic	4
Strong acids	TopH 5.0	—	Fish	Toxic	20
Cadmium chloride	0.01	Cd	Goldfish	Kills in 8-18 hrs	61
Cadmium sulfate	513	Cd	Minnows	Kills in 3 hrs	12
Copper sulfate	0.8	Cu	Goldfish	Kills in 24-96 hrs	24
Copper sulfate	0.04	Cu	<i>Daphnia magna</i>	Toxic	4
Sodium chromate	0.1	Cr	<i>Daphnia magna</i>	Toxic	3
Potassium dichromate	36	Cr	Goldfish	No effect in 108 hrs	24
Potassium dichromate	180	Cr	Goldfish	Kills in 3 days	24
Chromate (ion)	20	Cr	Trout and minnows	Kills in 8 days	28
Chromate (ion)	50	Cr	Sunfish, blue-gills	Not toxic in month	42
Chromate (ion)	0.01	Cr	Micro-flora	Toxic	29
Ferric chloride	34	Fe	Goldfish	Kills in 1-1.5 hrs	24
Ferrous sulfate	37	Fe	Goldfish	No effect in 100 hrs	24
Ferrous sulfate	368	Fe	Goldfish	Kills in 2-10 hrs	24
Nickel chloride	4.5	Ni	Goldfish	Kills in 200 hrs	24
Lead nitrate	63	Pb	Goldfish	Kills in 80 hrs	24
Stannous chloride	626	Sn	Goldfish	Kills in 4-5 hrs	24
Zinc sulfate	25	Zn	Trout	Kills in 133 mins	27
Zinc (ion)	0.3	Zn	Fish	Kills some fresh water fishes	54
Sodium cyanide	0.3	CN	Minnows, catfish, carp	No effect in 24 hrs	74
Potassium cyanide	0.04-0.12	CN	Goldfish	Kills in 3-4 days	24
Cyanogen chloride	0.08	CNCl	Fish	Critical	2
Potassium ferrocyanide	948	CN	Minnows, goldfish	Not lethal	59
Potassium ferricyanide	848	CN	Minnows, goldfish	Not lethal	59
Ammonia	2.5	NH ₃	Goldfish	Kills in 1-4 days	24
Ammonia	2-7	NH ₃	Fish	Lethal	20
Hydrogen sulfide	10	H ₂ S	Goldfish	Kills in 96 hrs	24
Sulfide (ion)	3	S	Trout	Kills in 5 mins	67
Sulfide (ion)	0.5-1.0	S	Fish	Critical	20
Potassium cyanate	264	KCNO	Trout fingerlings, adult minnows	No effect in 24 hrs	74
Sodium hydroxide	156	NaOH	<i>Daphnia magna</i>	Toxic	3
Trisodium phosphate	52	Na ₃ PO ₄	<i>Daphnia magna</i>	Toxic	3
Chlorine	0.05-1.0	Cl	Fish	Critical	20

**Daphnia magna* is a representative fish food organism commonly found in streams.

organisms which cause purification. The literature contains many references to difficulties caused by such polluting wastes in sewage treatment plants, but few basic investigations have been reported. The difficulties in establishing absolute toxicity limits for the various substances on these processes are just as great as those indicated in the discussion of toxicity to fish and fish food. Values reported in the literature for various com-

pounds are listed in Tables 4 and 5, but should be used conservatively for the reasons stated.

TABLE 4. EFFECT OF SOME COMPOUNDS ON ANAEROBIC DIGESTION

Substance	Concentration in sludge mixture		Effect	Ref.
	ppm	as		
Iron	—	—	Higher iron content caused faster digestion, but lowered gas production	34
Copper sulfate	(0.015%*)	Cu	No effect	74
	(0.030%*)	Cu	Reduced gas production to 12%	74
	(0.049%*)	Cu	Reduced gas production to 0.2%	74
Copper	150	Cu	Reduced gas production to 68%	70
	250	Cu	Reduced gas production to 0.5%	70
Copper hydroxide and copper sulfate }	200	Cu	Increased gas production somewhat	46
	200		Decreased gas production	46
Potassium cyanide	40	CN	Reduced gas production to 40%	21
Sodium cyanide	1.1	CN	No effect	68
Sodium cyanide	1.6	CN	Retarded gas production when first introduced, but did not reduce total gas production	68
Sodium cyanide	16	CN	No effect, if sludge is first acclimatized by low initial doses	68
Nickel	<500	Ni	Increases digestion activity, does not reduce gas production	29
	>500	Ni	Reduces gas production	29
Zinc	1,000	Zn	Critical limit	30

*Based on volatile matter in sludge.

TREATMENT PROCESSES

As has been previously emphasized, a complete survey of any individual plant and the wastes produced or likely to be produced should be made before selection of a method of treatment. The location of the plant with respect to other factories and population centers, and the nature of the sewage system or watercourse receiving the waste are other important factors. The detailed type of treatment ultimately recommended may therefore be expected to vary widely, and only general principles can be given in the discussion that follows.

Wherever possible, it is highly advisable to isolate the wastes containing cyanides and treat these separately from the other wastes, since the most effective methods of treatment for the two types of wastes are different. In addition, the danger of local acidification of cyanide wastes by acid wastes, with the consequent production of deadly hydrogen cyanide, is avoided. Separate lines should be used to carry the wastes to the collection points.

TABLE 5. EFFECT OF SOME COMPOUNDS ON AEROBIC PROCESSES

Substance	Concentration in sewage mixture (ppm) as		Process Type	Effect	Ref.
Chromic acid	4.68	Cr	Filters	Stopped biological action entirely	76
Potassium dichromate	1.0	Cr	Filters	Hardly affected nitrification	40
	10	Cr	Filters	Reduced nitrification somewhat, and lowered quality of effluent	40
	100	Cr	Filters	Nitrification reduced 66-78% and organic matter increased 186-242% in effluent	40
Sodium or potassium cyanide	2.0	CN	Filters	Reduces nitrification	60, 66
Sodium or potassium cyanide	9.7	CN	Filters	Effluent quality decreased but recovered quickly when cyanide addition was discontinued	66
Sodium or potassium cyanide	29	CN	Filters	Effluent quality first decreased but at end of three weeks was as good as control, even with continued cyanide addition	66
Sodium cyanide	2.0	CN	Activated Sludge	Reduced nitrification somewhat	69
Sodium cyanide	40.0	CN	Activated Sludge	Reduces but does not completely prevent nitrification. Quick recovery after cyanide removal	69
Potassium cyanide	330	KCN	Activated Sludge	No effect, if acclimatized first	55
Nickel sulfate	1	Ni	Activated Sludge	Inhibited nitrification	36
Nickel sulfate	10	Ni	Activated Sludge	Has pronounced effect	36
Ferric chloride	9 to 500 ppm		Activated Sludge	Retarding effect	53
Ferric sulfate				Retarding effect	53
Aluminum salts				Retarding effect	53
Boron	1	B	Activated Sludge	Sludge will not settle	58

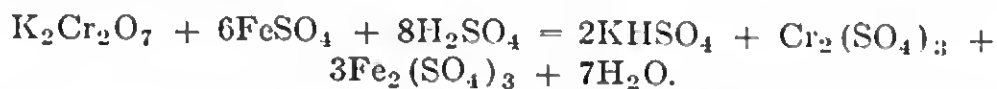
Treatment of Wastes not Containing Cyanides

The most important constituents of these wastes are acids used for pickling and cleaning (such as sulfuric, nitric, and hydrochloric acids), alkaline cleaners, chromate anodizing or pickling or plating wastes, wastes from nickel-plating baths and other types of plating which do not use cyanides, and usually some oil and grease from cleaning processes. As a result of the various cleaning and plating operations, the baths will contain heavy metals, the most common ones being copper, iron, zinc, aluminum, and nickel, as well as chromium in both the hexavalent and trivalent form. Partial neutralization will, of course, occur through the mixing of

these various types of liquids, but the over-all waste is almost always acidic. Any treatment process is thus designed to neutralize excess acidity and remove the metallic ions. In most cases the metallic ions are apparently sufficiently removed as hydrous oxides by bringing the pH of the mixture to 8. The addition of aluminum or ferric sulfate as a carrier when the metallic content is small is sometimes recommended. Since chromate ions will not be removed by precipitation under these conditions, special treatment for wastes containing hexavalent chromium is necessary.

In some plants where large amounts of relatively concentrated sulfuric, nitric, and hydrochloric acid wastes are disposed of, these solutions are collected separately from the chromate wastes and neutralized with lime. The sludge, which contains calcium sulfate and hydrous oxides of the heavy metals, is led to lagoons.³² In the average plating plant, however, this separation is not practical. In such a case, when concentrated acid (or alkaline) baths are dumped, they should be proportioned into the more dilute wastes.

One of the most successful methods for the treatment of wastes containing chromates has been the reduction of the chromate ion by ferrous sulfate, followed by neutralization with lime to precipitate the various heavy metals. The reaction occurring in the presence of excess mineral acid may be written as follows:



In this reaction, 16.04 parts by weight of copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) are required to reduce one part of Cr from the hexavalent to the trivalent condition. Grindley²⁸ has made a thorough examination of the use of this process to treat chromate wastes. With dilute chromate solutions (20 ppm as Cr) the reaction is rather slow if stoichiometric equivalents are mixed. With twice the calculated amount of ferrous sulfate, however, the reaction is more rapid and may be assumed to be complete in one hour or less. For solutions containing higher concentrations of chromate (about 500 ppm as Cr), reduction is apparently complete in one hour if the theoretical amount of ferrous sulfate is added. The reaction has been shown to take place equally well in waste solutions which are originally acid and those with an original pH up to 10. After complete reduction of the chromate, the solution is made alkaline to pH = 8 by the addition of milk of lime, and the heavy metals thus precipitated as hydrous oxides.

For the actual treatment, the batch-type process should be used if possible. Barnes has described an installation of this type at a plant in Meadville, Pa.⁵ Acid-resisting tanks should be provided, preferably in units of three, to allow one day for collection, a second for treatment and

settling, and a third for run-off at a controlled rate. The tanks should be equipped with suitable mixers, baffled decanting outlets, skimmers, and sludge outlets. The treatment chemicals may be stored in bins and mixed in solution tanks. The waste is treated with from one to two times the theoretical amount of copperas and mixed thoroughly. After allowance of one hour for complete reduction, oil and grease may be taken off the top if necessary. Milk of lime is then added to pH = 8. The mixture is again agitated, and allowed to settle, preferably overnight. The supernatant liquor is then decanted and the sludge drawn off. Adequate controls should be established over the various steps in the process. A similar treatment has been employed in other plants.^{26,32}

If very large amounts of wastes are to be treated, it may be possible to employ a continuous treatment process, but this is usually not satisfactory if there is a large variation in the acidity and nature of the wastes. Keleh and Graham⁴¹ have described a plant of this kind in which the addition of copperas is controlled by a pH meter and a platinum-calomel electrode system. It may also be possible to use alkaline wastes from other parts of the plant (such as the effluent from alkaline chlorination of cyanides) for neutralization of acid wastes in this treatment, but this has not yet been fully investigated.

The type of results obtained at one plant in Connecticut with the ferrous sulfate process is indicated in Table 6.

TABLE 6. FeSO_4 TREATMENT OF PLATING WASTES
(Analyses in ppm of substance indicated)

	Influent	Effluent
pH	11.9	7.3
Cu	21	13
Fe	16	10
Ni	24.1	0.5
Cr^{6+}	70.0	0.0
Cr_{total}	73.7	0.6
CN	13	13

Excellent results on the removal of chromate and nickel have consistently been obtained at this plant. The reduction in copper is not as satisfactory, but this is to be expected because of the presence of cyanide ion in the waste. Because of poor testing methods, the regulation of the pH of the mixture after the addition of ferrous sulfate has not been carefully controlled at this plant. At one factory in Pennsylvania it is reported⁵² that the average waste containing 100 ppm chromium, 10 ppm cadmium, and 3.0 ppm copper shows no amounts of these metals within titratable limits in the effluent. This particular effluent is discharged into a tributary

of a stream used as a public water supply and has been consistently checked by responsible agencies in the area.²⁶ Results on the removal of zinc have apparently not been reported from any plant. Grindley has shown that undiluted samples of waste water which had been treated with ferrous sulfate had no apparent effect on minnows in exposures up to two days.²⁸

Metallic iron, usually in the form of scrap steel, has been used as a reducing agent in a number of cases.^{6,28,37} However, chromate ion in the higher concentrations often found in plating wastes tends to make the iron passive. With small amounts of chromates, the reaction is very slow unless an excess of mineral acid is present ($\text{pH} < 3$). Ferrous sulfate, on the other hand, may be used for solutions of pH at least up to 10.

Recently there has been a tendency to replace copperas as a reducing agent by sulfur dioxide. Only 1.9 parts of sulfur dioxide are required to reduce one part of hexavalent chromium, as contrasted with 16 parts of copperas. This substance may be added directly as a gas or liquid^{37,79} or through various solid compounds such as sodium hydrogen sulfite^{63,75,87} or sodium dithionite.⁷⁸ At one plant in Connecticut sodium pyrosulfite (also called sodium metabisulfite, $\text{Na}_2\text{S}_2\text{O}_5$) has been used for about a year with good success. It is claimed that this material is a cheaper source of sulfur dioxide than the gas and it is somewhat easier to handle and control. One part of hexavalent chromium requires 2.8 parts of sodium pyrosulfite for reduction. Treatment with sulfur dioxide in any of the various forms requires a pH of less than three. This process is then followed by neutralization to remove excess acidity and precipitate the metallic ions. Careful control is obviously necessary to avoid excess sulfur dioxide.

Barium sulfide was used fairly successfully for a number of years in one plant in Connecticut.³⁷ In this case the chromate was partially reduced and partially precipitated as barium chromate. The pH must be below 3 when the barium sulfide is added, and this treatment is therefore followed by the addition of lime to $\text{pH} = 8$ to remove heavy metals. However, the process requires greater care in operation particularly to avoid the presence of hydrogen sulfide in the effluent. There is also the danger of introducing excess barium, which is itself poisonous. This excess may be controlled by the addition of ferric sulfate or sodium carbonate. Barium chloride has been used to precipitate chromate, followed by addition of sodium carbonate to remove excess barium ion and precipitate the heavy metals as basic carbonates.⁷⁶ This process is open to some of the same objections as the barium sulfide method.

An interesting method has been reported from England²⁸ in which a suspension of barium carbonate in the form of finely ground witherite

has been used to precipitate chromate and sulfate. The reaction rests on the fact that barium chromate and barium sulfate are more insoluble than barium carbonate. With this method a continuous process and unskilled labor may be used for the chromate removal, but it would be necessary to employ subsequent treatment with alum or sodium sulfate and alum, if the waste waters contained free acids of which the barium salts are soluble. Heavy metals such as copper and zinc are not removed appreciably, and this would require further treatment with lime or sodium carbonate.

Dodge and co-workers have published extensive reports on the recovery of metals from wastes in the copper and brass industries.⁸⁵ They show that, at least in one plant, 90 per cent of the wasted material comes from the large volume of flow of the relatively dilute rinse solutions. These rinse solutions are, however, usually more concentrated, particularly with respect to copper and zinc, than the average trade wastes from a plating plant. Other studies of the possibilities of recovery or regeneration of chromate- and copper-containing wastes have also been made.^{37,47} Due consideration to such possibilities should be given in the study of any treatment plant, but there does not appear to be any case in which the application of such methods to the wastes actually discharged in a plating plant has yet been economically solved. As has been indicated before, recovery of expensive metals such as gold, silver, platinum, and rhodium is commonly practiced, but solutions containing these metals are carefully excluded from the general waste waters.

One method which may offer promise for the future in the treatment of plating wastes and the recovery of valuable constituents, is the use of ion-exchange materials. However, this process is still in the research and development stage. There have been many applications of this type of procedure in the recovery of copper from rayon wastes, with essentially complete removal of the copper. Preliminary studies have also been made of the application to wastes from the brass and copper industries,^{7,86} and it has been indicated that the regenerated solution from such a process may be concentrated to about 2,000 ppm of copper and 2,000 ppm of zinc. Difficulties have been cited in attempts to regenerate chromate ions after removal,^{10,11,28,86} but these were reportedly overcome in one case by proper choice of ion-exchange material and regenerant.⁷⁷ It is possible that the future may see a battery of ion-exchange beds operated on a countercurrent principle employed for the solution of the recovery and trade-waste problems in much of the plating industry. It should be noted, however, that ion-exchange materials merely serve to concentrate the wastes and do not dispose of them.

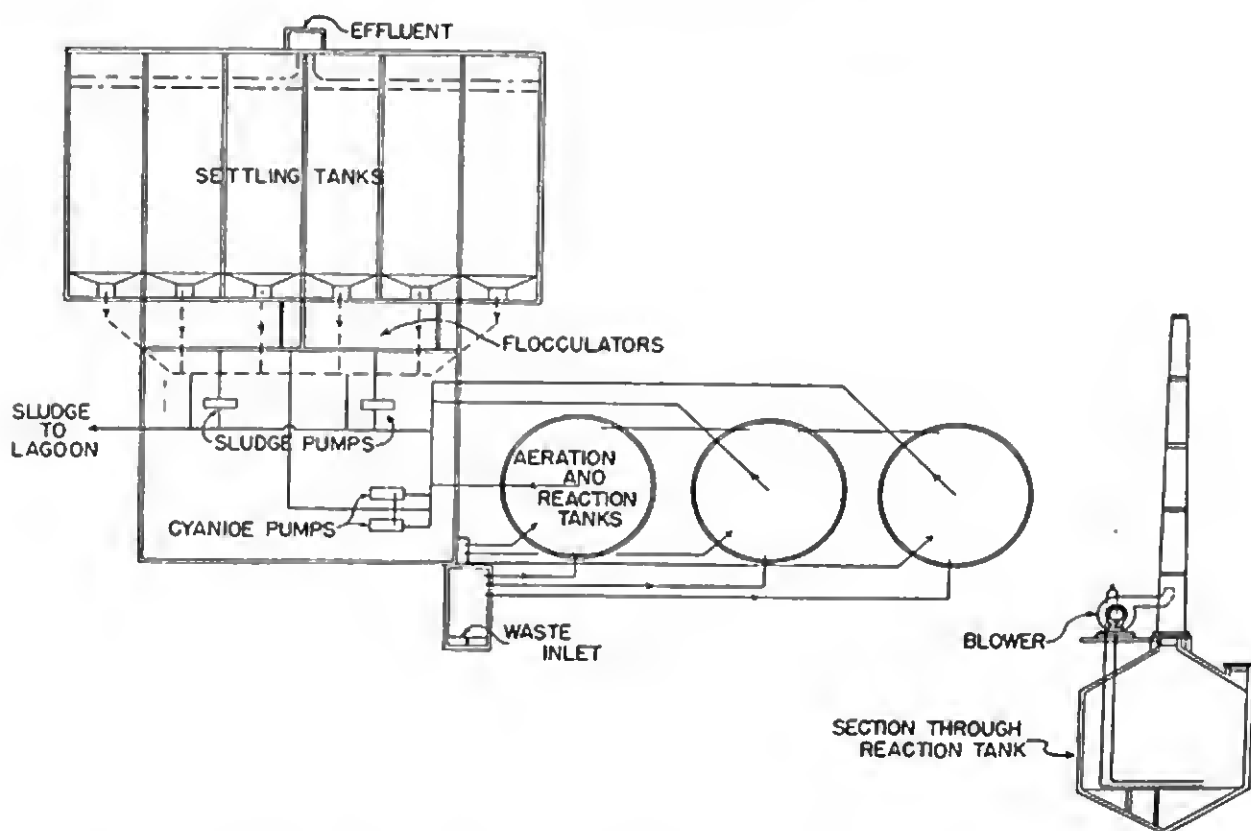
Cyanide Waste Treatment

Methods for the removal and recovery of cyanides from trade wastes have been under sporadic investigation since about 1909, but it is only since 1933 that more detailed consideration has been given to the problem. Dodge and Reams¹⁹ have published an extensive critical review of the literature in this field. Only the more important methods will be considered in the present discussion. It should be emphasized again that a thorough survey of the plant under consideration is necessary before a definite method of treatment is adopted. In addition, different methods of treatment for concentrated and dilute cyanide wastes may sometimes be advisable.

Acidification and Aeration. Ponding of cyanide wastes and allowance for natural aeration is the simplest possible method of treatment, but is not generally satisfactory. It has been shown that approximately nine days are required for the removal of cyanides from neutral wastes by this process.¹³ Wastes containing up to 100 ppm of cyanide which are acidified to a pH of less than 3 will lose about 75 to 85 per cent of their cyanide content in 48 hours' detention in lagoons of about two foot depth. No studies have apparently been made of the time necessary for complete removal of cyanides under these conditions. The process is almost entirely one of evolution of hydrocyanic acid from the acid solutions.

Since large areas of land are required, and because of the dangers involved, this method should be employed only in relatively isolated sections. The lagoons should be baffled and they should be fenced in and warning signs posted. Care must be taken that there is no underground seepage to water supplies, and this may require the building of concrete bottoms for the lagoons. The effluent should be carefully tested before discharge to any watercourse, and should be discharged only if sufficient water is available in the stream to provide dilution of the cyanide content, preferably to 0.05 ppm or less, but this depends on the particular stream and its uses. The process is at best a poor one, and should be employed only if other methods are not possible.

Acidification in plant installations, followed by enforced aeration through a tall stack, is far superior to ponding and has proved feasible in many cases. The process was originally developed for the recovery or removal of cyanides from concentrated solutions³¹ and was applied by Eldridge^{21,22} to plating wastes. An installation of this type has been in operation at the Chevrolet Division of General Motors Corporation in Flint, Michigan, since 1934. Herda³³ has described a similar installation in the Willow Run Plant now operated by the Kaiser-Frazer Corporation (Figures 2 and 3).



(Courtesy N. Herda)

FIGURE 2. Diagrammatic lay-out for cyanide and acid plating waste treatment plant, Kaiser-Frazer Corp., Willow Run, Michigan



(Courtesy N. Herda)

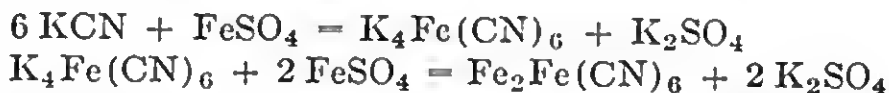
FIGURE 3. Exterior view of cyanide and acid plating waste treatment plant, Kaiser-Frazer Corp., Willow Run, Michigan

Because of the toxic nature of the hydrogen cyanide produced on acidification of cyanide wastes, great care must be taken in the location, design, and operation of such plants. The wastes are led directly to tanks large enough to hold a day's supply of wastes. The tanks may be constructed of rubber-lined steel or other acid-resistant material. They should be tightly sealed, cone-shaped at the top, and provided with a stack from 40 to 100 feet high, depending on the location. The bottoms of the tanks are provided with air-diffusion apparatus, and the fumes are forcibly vented from the stack by high-capacity blowers to supply sufficient dilution for the poisonous hydrogen cyanide. (The Willow Run plant provides 5,000 cubic feet per minute.) The tank is filled with waste, the cyanide content determined, and sufficient sulfuric acid added through perforated lead pipes above the solution level to reduce the pH of the waste to a value of 3 or less. The acid should be added slowly, particularly to the more concentrated wastes, to avoid the sudden evolution of more hydrogen cyanide than can be sufficiently diluted by the blower system. The solution is aerated and the fumes forcibly vented until the cyanide content has been reduced to 1 ppm or less. This process requires from 6 to 16 hours depending on the original cyanide content and the efficiency of the aeration and blower system. Highly acid residues, and those containing appreciable quantities of metals should be neutralized with lime or sodium hydroxide before admission of the effluent to a stream or sewage system. It should be noted that solutions containing silver and copper will not release all their cyanide on acidification but retain some of it with the formation of insoluble residues.

In a typical operation at the Chevrolet plant,²² 4,500 gallons of waste copper plating solution containing 15,200 ppm cyanide as NaCN was treated with 4,255 lbs of 66° Baumé sulfuric acid and aerated for 16 hours. The cyanide content was reduced to about 1 ppm. At Willow Run³³ about 60,000 gallons of cyanide wastes per month, containing about 75 ppm of cyanide, and with an original pH of 10, were treated with about 14 lbs of sulfuric acid per pound of cyanide. The final waste, after neutralization, contained about 1 ppm cyanide and had a pH of 7.

It should be noted that this process produces an effluent which contains about 1 ppm of cyanide and that subsequent disposal should therefore provide a dilution of one to twenty for complete safety if the effluent is led to a stream and on to a sewage system. Tests should be carefully made to be sure that the vented vapors do not contain dangerous quantities of hydrogen cyanide. The use of this process in highly populated areas is questionable, but there is no evidence of actual danger resulting from the carefully controlled process. The problem involved appears to be one of psychology and public relations. The method may not be sufficiently efficient for treatment of dilute wash solutions.

Treatment with Ferrous Sulfate. This process, which has already been discussed under the removal of metals from plating wastes, is one of the oldest methods proposed for the removal of cyanides.^{15,51} The nature of the precipitate produced will vary with conditions. Possible reactions are as follows:



The ferrous ferrocyanide thus produced may be converted by metathetical reaction, by means of ferric ions either present in the waste as such or produced by oxidation of ferrous ions, to ferric ferrocyanide, a form of Prussian Blue:



A careful study of the conditions necessary for the removal of cyanide by ferrous sulfate has been published in England.⁶⁴ Experiments were carried out on solutions containing potassium cyanide, sodium zinc cyanide, sodium cuprocyanide and mixtures in concentrations equivalent to 10 to 100 ppm of HCN. It was found that maximum precipitation of cyanide occurred only if sufficient lime was added to the mixtures to yield a pH between 7.5 and 10.5. Excess ferrous sulfate is necessary, particularly for mixtures containing cuprocyanides, where 16 moles of ferrous sulfate were added per mole of cyanide in a plant scale treatment. Reductions in cyanide ran between 88 and 96 per cent, producing effluents containing from 2 to 6 ppm of "free" HCN under ideal conditions. Poor results were obtained with samples originally containing 10 ppm or less.

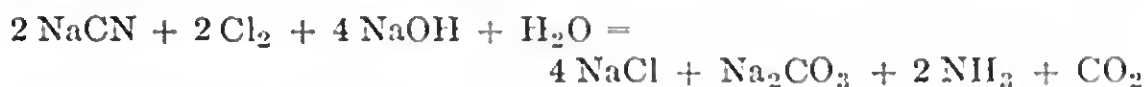
This process requires careful and intelligent chemical control, particularly with wastes which show large variations in composition. In actual plant experience in Connecticut, where a similar process is carried out primarily as a means of removing chromate under routine control, the cyanide reductions (original concentration 13 ppm, see Table 6) have been negligible. The large volume of highly-colored sludge produced might also be objectionable. In general the residual cyanide content is too high for safe disposal of the wastes to streams, and recent experience has indicated the abandoning of this process as a means of removing cyanide, particularly in favor of alkaline chlorination.⁴⁸

Alkaline Chlorination. The alkaline chlorination treatment of cyanide wastes is apparently the most generally satisfactory method so far devised. Chlorination was originally suggested by Moir and Gray^{50,51} and tested by Eldridge,²¹ but unfortunately the process was carried out in acid solution, and under those conditions the reaction product was cyanogen chloride, which was about as toxic as hydrogen cyanide. Dodge and

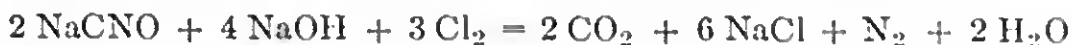
Reams¹⁸ point out that White,⁸² in a discussion of Moir and Gray's papers, indicated the reaction of chlorine with cyanide in alkaline solution to form cyanates.

The basis for the modern alkaline chlorination method apparently lies in a patent by Heuser³⁵ for the preparation of cyanogen chloride. Oeming⁵⁶ states that a patent application for alkaline chlorination of cyanide wastes was made in 1939 but later rejected. In 1941 Bezzubets and Vozhdayeva reported good results with sodium hypochlorite,⁹ and Schulenberg and Beier obtained a German patent involving the process in the same year.⁷⁵ In 1942, following a suggestion by Faber, Friel and Wiest, with Metcalf and Eddy, developed the first practical application of the method in this country.²⁶ Dobson has given a comprehensive discussion of the process.¹⁶

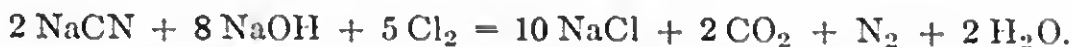
The exact nature of the reaction taking place in the chlorination of cyanides in alkaline solutions has not yet been worked out. Friel and Wiest²⁶ give an over-all reaction of



and indicate the formation of cyanogen chloride and sodium cyanate as intermediates. However, it is well known that ammonia reacts rapidly with chlorine to produce chloramines and finally nitrogen, so that this equation does not seem probable if residual chlorine is found in the reaction mixture. Dobson¹⁶ states that the reaction takes place in two steps:



These would give the following over-all reaction:



According to Dobson the first reaction is practically instantaneous but the second reaction occurs much more slowly so that it is possible to stop with the formation of cyanate. It is indicated that oxides of nitrogen may also be formed in the over-all reaction. Price and co-workers⁶² have studied the kinetics of the reaction between cyanides and chlorine. They report the following reactions at pH = 8:



The first reaction is very rapid; the second is almost complete in ten minutes and complete in one-half hour, with concentrations similar to those found in trade wastes. From investigation of the chlorinolysis of

cyanates the authors report that the second reaction involves an instantaneous conversion of cyanogen chloride to cyanate, followed by reaction to yield carbon dioxide and nitrogen. The ratios of chlorine to cyanide and cyanogen chloride bear out the stoichiometry of this reaction. Further kinetic studies have been carried out in England.⁶⁵

If the above reactions are combined and the "active" chlorine source written as chlorine and sodium hydroxide rather than hypochlorous acid, the same over-all equation is obtained as in Dobson's reaction. Experiments carried out in this laboratory using the "break-point" technique of chlorination confirm the over-all reactions of Dobson and Price, but also indicate the formation of ammonia and chloramines as intermediates in the reaction.⁴⁴ In some of these experiments a precipitate of calcium carbonate was obtained within 4 or 5 seconds after the addition of chlorine as a bleaching powder. Maximum removal of cyanide was obtained by adding enough chlorine to completely oxidize the cyanide to carbon dioxide and nitrogen.

The theoretical requirement for reaction to form cyanates is 2.7 parts of chlorine and 3.1 parts of sodium hydroxide (by weight) per part of cyanide as CN. For the over-all reaction to nitrogen and carbon dioxide, 6.8 parts of chlorine and 6.2 parts of sodium hydroxide are required per part of CN. Although oxidation to cyanate is sufficient to reduce the toxicity of the effluent in some cases, since cyanates are only about one thousandth as toxic as cyanides, it is probably safer to carry the reaction all the way to nitrogen and carbon dioxide. The solution must be kept alkaline at all times to avoid the formation of nitrogen trichloride. A maintained pH about 8.5 is probably sufficient for this purpose, but a value of greater than 11 has also been recommended.^{1,65} Much of the required alkalinity will be present in the wastes. The temperature should be kept below 50°C, since chlorine will react above this point to form chlorates. Since the oxidation of cyanide to cyanate is exothermic, the chlorine should be added slowly or provision should be made to keep the temperature sufficiently low.¹⁶

For small and medium sized plants, batch-treatment installations are probably best. The cyanide wastes should be kept separate from the acid wastes. The rinse waters from alkaline cleaners may be added to the cyanide wastes or used for partial acidification of the acid wastes. The former process will probably increase the chlorine demand. At least two and perhaps three wooden storage tanks should be provided, each of large enough capacity to hold a day's wastes in addition to the volume of treatment solutions needed. This will allow one day for storage, one for transfer and treatment, and a third, if necessary, for release of the treated wastes at a slow rate into the sewer or stream.⁵

The pH of the solution is raised to beyond 8.5 and maintained at this point by addition of lime or sodium hydroxide. A greater amount of sludge will of course be produced if lime is used. Adequate provision must be made for mixing. The determination of the amount of chlorine necessary for oxidation of the cyanide and the detention time required must always be made by actual measurements on the plant wastes since these will vary with the type of waste. In most cases a detention time of 20 to 60 minutes appears to be sufficient. For small scale work, the chlorine may be added in the form of bleaching powder (app. 30 per cent available Cl_2). This has the added advantage of supplying its own alkalinity, but with concentrated solutions a large amount of sludge is obtained. The powder should be added slowly to avoid excessive foaming. Alternatively, the waste may be pumped through the injector of a chlorinator. In any case, adequate mixing must again be provided, and the usual precautions in the use of chlorine observed. Barnes⁵ has described a modern installation of this type. As an added precaution against the formation of nitrogen trichloride, the tanks are hooded and the top gases exhausted to an absorption tower. The small amount of sludge usually formed is drawn off to a sludge well and combined with sludges from other treatment processes.

For cases where the large amounts of waste discharged make batch treatment impractical, Dobson¹⁶ has described a continuous treatment plant with automatic controls (Figure 4). In this case the concentrated wastes are collected separately and proportioned into the dilute waste stream. The addition of alkali is controlled by a pH recorder located beyond the point of chlorination. For wide variations in the rate of flow, an automatic chlorinator is recommended. Pumped plant effluent is used for the operation of the chlorine injector. If the oxidation is carried to the formation of nitrogen and carbon dioxide a series of reaction chambers should be used, and these are also advisable if there is a wide variation in the cyanide content. The plant is designed to take care of a flow of 400 gpm of waste containing 100 ppm of CN.

Results of this method of treatment of cyanide wastes have been very promising so far although operating data are meager. Barnes⁵ reports that treatment of an average of 14,716 gallons of waste daily containing 212 ppm of CN gave an average content of 2.5 ppm after chlorination and 1.2 ppm after the addition of excess lime to remove copper. It should be noted, however, that there was no residual chlorine content in the effluent, and the average pH after chlorination was 7.5. Friel and Wiest²⁶ report "complete" removal of cyanide and it has also been stated that no chromium, copper, or cadmium within titratable limits was present.⁵² Dobson¹⁶ states that, in all trade wastes and laboratory samples tested, no cyanide within the limits of titration accuracy has been found in the

presence of free available chlorine at pH 8.5. Results in this laboratory⁴⁴ have indicated a maximum of 0.2 ppm in all samples in which sufficient chlorine was added to oxidize the cyanide to nitrogen and carbon dioxide. In most cases no detectable cyanide was present. There have been numerous recent indications of successful operation at various plants on both concentrated and dilute cyanide wastes.^{63,79,83} Chlorine gas, sodium

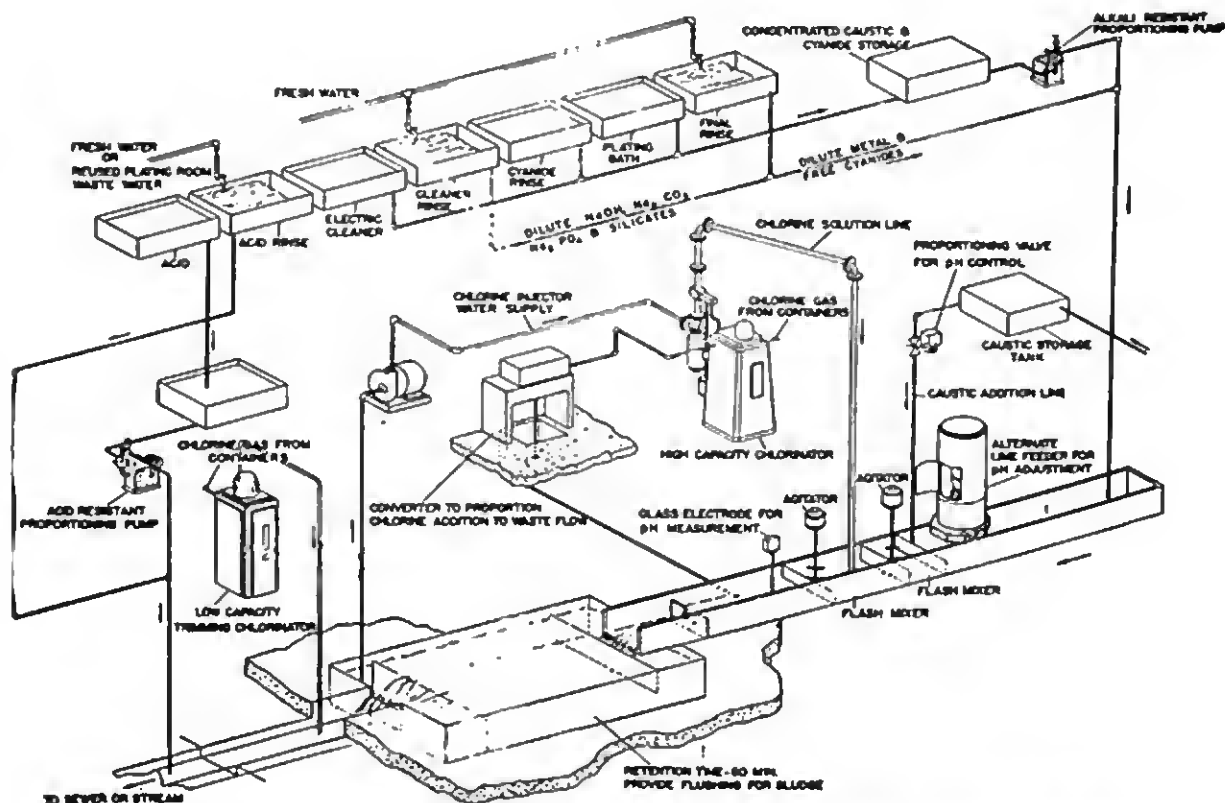


FIGURE 4. Schematic layout—continuous treatment plant—cyanide wastes¹⁶

hypochlorite and bleaching powder have all been used as the chlorine source.

Beier⁷⁵ points out that the effluent from the chlorination process may be used to neutralize acid wastes. Any cyanates present would then be changed to carbon dioxide and ammonium ion. The original patents provided for the recovery of copper which would be precipitated as basic carbonate in the chlorination treatment. Zinc can be removed by suitable adjustment of the pH of the effluent. It might also be possible to work out a method to recover silver as chloride or oxide, but the possibility of the formation of explosive compounds of silver in this chlorination reaction should be fully investigated since ammonia is one of the intermediates in the reaction. For most types of wastes in the plating industry it is doubtful whether the expense of recovery would be justified by the small amounts of cadmium, zinc or copper obtained.

The effect of chlorinated cyanide wastes on fish was investigated by Washburn.⁸⁰ He found that dilution ratios of 200 to 1 were necessary to render the effluents harmless but the solutions used in these experiments were much higher in concentration than the usual plating wastes. Moreover, there was a high value of residual chlorine in two of his test solutions and such a residual should be avoided if the treated wastes are to be admitted to a stream, since from 0.5 to 1.0 ppm of chlorine has been shown to be toxic to *Daphnia magna* and fish.²³ The excess of chlorine can be removed by an agent such as sodium acid sulfite. In addition, since monochloramine is toxic to trout in concentrations as low as 0.06 ppm,¹⁴ this may be considered as a further reason for chlorination to carbon dioxide and nitrogen rather than simply to cyanate formation.

Other Methods. Numerous other types of methods have been proposed. Precipitation of the cyanide by zinc⁵¹ or copper²⁵ is possible, with or without subsequent evolution or absorption or hydrocyanic acid. However, these methods are generally applicable only to concentrated solutions and do not accomplish complete removal of the cyanide.

Oxidation of cyanide in neutral or alkaline solution by potassium permanganate has been shown to be feasible.^{21,50} The reaction occurring is:



The residual cyanide is one part per million or less, and according to Hubbs³⁸ the toxicity level of cyanate to shiners is 125 to 250 ppm, so that dilution of the waste effluent with about twenty volumes of water should remove all ordinary dangers. However, although installation costs for such a treatment would be relatively low, operating costs are high, and sludge disposal is necessary. There are apparently no practical applications of this method.

When alkaline cyanide solutions are heated to about 80°C and commercial lime-sulfur spray material (essentially calcium polysulfide) is added, the cyanides are converted to the less toxic thiocyanates. This process is the basis of a patent issued to Wernlund and Zunick.⁸¹ An essentially similar process occurs to some extent in the treatment of cyanide-containing chromate wastes with barium sulfide as recommended by Hoover and Masselli.³⁷ In the lime-sulfur treatment about 1.84 lbs of solid calcium polysulfide are required per pound of sodium cyanide.^{22,56} The reaction takes about 30 minutes at high temperatures and 2 hours at ordinary temperatures.

According to the original patent the cyanide content may thus be reduced to about 4 ppm as sodium cyanide, and excess sulfide can be removed by precipitation with ferrous sulfate.⁸¹ However, in actual installations and applications to zinc and copper plating wastes the effluents contain from 100 to 300 ppm of sodium cyanide.^{68,69} Ridenour

and co-workers have shown that the wastes from such a treatment plant will not seriously affect aerobic and anaerobic digestion in sewage plants.^{68,69} The process requires only inexpensive equipment and is relatively easily controlled. However, the cyanide content of the effluent is too high to allow safe discharge with most available dilutions and the effluent contains a high content of sulfide, which is also toxic. There is danger of the evolution of hydrogen sulfide if the effluent comes in contact with acids and the process is not applicable to dilute rinse solutions such as those found in plating wastes. If the effluents reach the chlorination type of sewage treatment plant, chlorine will react with the thiocyanates to produce the highly toxic cyanogen chloride.⁵⁶

Electrolytic oxidation of cyanide wastes to cyanates and perhaps other compounds has been proposed at various times and some recent papers in this field have appeared.⁵⁷ The method may be applicable to concentrated wastes under specialized conditions, but a high concentration of cyanates is produced which would require subsequent destruction.

Milne⁴⁹ has proposed the formation of complex cyanides by combination with nickel wastes, and Dodge and Reams¹⁷ refer to unpublished work from the du Pont Company on evaporation of concentrated solutions and heating to dryness at elevated temperatures. The latter method may be applicable in certain cases to solutions containing more than 5 per cent of sodium cyanide.

Some work has been reported on the application of ion-exchange resins to the concentration of cyanide solutions¹⁰ but difficulties were encountered in the recovery of cyanide and regeneration of the resin. Losson and Bloodgood also describe a method by which the metallic ions are removed on a resin and the cyanide by aeration and absorption of the hydrocyanic acid in sodium hydroxide solution for recovery.⁴⁵ Further work in the ion-exchange field is needed, but it should again be emphasized that this involves concentration of the wastes rather than disposal.

References

A very complete bibliography of the disposal of plating wastes has been published by the American Electroplaters' Society as A. E. S. Research Report, Serial No. 9 by B. F. Dodge and D. C. Reams. This covers through 1947 and part of 1948. Only references pertinent to the discussion in this chapter are given below.

1. "Alkali Chlorination Method for Cyanide Waste Disposal," Mimeographed leaflet of E. I. du Pont de Nemours and Co., Niagara Falls, N. Y.
2. Allen, L. A., Blezard, W., Wheatland, A. B., *J. Hyg.*, **46**, 181-93 (1918).
3. Anderson, B. G., *Sewage Works J.*, **18**, 82-87 (1946).
4. Anderson, B. G., *Sewage Works J.*, **16**, 1156-65 (1944).
5. Barnes, G. E., *Water and Sewage Works*, **94**, 8 (1947); Proc. 3rd Ind. Wastes Conf., Purdue Univ., 179-91 (1947).

6. Barnes, G. E., and Braidech, M. M., *Eng. News-Record*, **129**, 496-99 (1912).
7. Beaton, R. H., and Furnas, C. C., *Ind. Eng. Chem.*, **33**, 1500-13 (1941).
8. Belding, D. L., *Trans. Am. Fisheries Soc.*, **57**, 100-19 (1927).
9. Bezzubets, M. K., and Vozhdayeva, V. N., *J. Gen. Chem. Ind. (U.S.S.R.)*, **18**, 17 (1941); *Chem. Zentr.*, 1942, II, 2833; *C.A.*, **38**, 2777 (1944).
10. Bloodgood, D. E., and Losson, F. J., Jr., *Proc. 3rd Ind. Waste Conf., Purdue Univ.*, 196-208 (1947).
11. Bloodgood, D. E., and Strickland, A., *Water and Sewage Works*, **97**, 28-32 (1950).
12. Carpenter, K. E., *British J. Exp. Biol.*, **4**, 378-90 (1927). Cited by Ellis, M. M., *U. S. Bur. Fisheries Bull.*, **48**, 421 (1940).
13. Clevenger, G. H., and Morgan, H., *Mining Sci. Press*, **113**, 413-23 (1916); *C.A.*, **10**, 2861 (1916).
14. Coventry, F. L., Shelford, V. E., and Miller, L. F., *Ecology*, **16**, 60-66 (1935).
15. Denis, J., British Patent 250,824 (1924). *C.A.*, **21**, 1321 (1927). Hoover, C. R., Biennial Rep't. State Water Comm. Connecticut, **5**, 45 (1934). Strell, M., *Gesundh.-Ing.*, **62**, 546-50 (1939); *C.A.*, **34**, 560 (1940). Barnes, G. E., and Braidech, M. M., *Eng. News Record*, **129**, 496-99 (1912).
16. Dobson, J. G., *Sewage Works J.*, **19**, 1007-20 (1917); *Metal Finishing*, **45**, 2, 78-81; No. 3, 68-71 (1947).
17. Dodge, B. F., and Reams, D. C., Ref. 19, pp. 29-30.
18. Dodge, B. F., and Reams, D. C., Ref. 19, p. 17.
19. Dodge, B. F., and Reams, D. C., American Electroplaters' Society Research Report, Serial No. 14, American Electroplaters' Society, Jenkintown, Pa. (1949).
20. Doudoroff, P., and Katz, M., *Sewage and Ind. Wastes*, **22**, 1432-58 (1950).
21. Eldridge, E. F., Mich. Eng. Expt. Sta. Bull. No. 52 (1933).
22. Eldridge, E. F., Mich. Eng. Expt. Sta. Bull. No. 60 (1934); "Industrial Waste Treatment Practice," pp. 288-99, New York, McGraw-Hill Book Co., Inc. (1942).
23. Ellis, M. M., *U. S. Bur. Fisheries Bull.*, **48**, 421 (1940).
24. Ellis, M. M., *U.S. Bur. Fisheries Bull.*, **48**, 365-437 (1940). (Bull. 22, 1937).
25. Ewan, T., and Lemmon, R. J., U. S. Patent 1,992,060 (1935); *C.A.*, **29**, 2139 (1935).
26. Friel, F. S., and Wiest, G. J., *Water Works and Sewerage*, **92**, 97-8 (1945).
27. Grindley, J., *Am. Applied Biol.*, **33**, 103-12 (1946); *C.A.*, **40**, 5178 (1946).
28. Grindley, J., *J. Soc. Chem. Ind.*, **64**, 339-44 (1945).
29. Grushko, Y. M., *Gigieno i Sonit.*, 1950, No. 2, 17-19; *C.A.*, **44**, 5013i (1950).
30. "Guidebook and Directory for the Metal Finishings Industries," pp. 41-78. New York, Metal Industry Publishing Co. (1917).
31. Halvorsen, A. L., Canadian Patent 237,616 (1924); *C.A.*, **18**, 1037 (1924). U.S. Patent 1,486,137 (1924); *C.A.*, **18**, 1553 (1924). Burk, H. A., and Pettis, E. S., *Mining and Met.*, **6**, 136-143 (1925); *C.A.*, **19**, 3079 (1925). Oesterreichisch-Alpine Montangesellschaft, Austrian Patent 118,009 (1929); *Chem. Zentr. II*, 1262 (1930). British Patent 353,184 (1929); *C.A.*, **26**, 2809 (1932). French Patent 702,520 (1930); *C.A.*, **25**, 4338 (1931). Bryan, R. R., U.S. Patent 1,787,033 (1930); *C.A.*, **25**, 780 (1931). Mills, L. D., and Crowe, T. B., U.S. Patent 1,809,248 (1931); *C.A.*, **25**, 4213 (1931).
32. Herda, N., *Sewage Works J.*, **18**, 499-502 (1946).
33. Herda, N., Ref. 32. See also Fadgen, T. J., *Proc. Am. Electroplaters' Soc.*, **28**, 44-6 (1940); *Proc. 2nd Ind. Waste Conf., Purdue Univ.*, 167-72 (1946).
34. Heukelekian, H., N.J. Agr. Expt. Sta. Bull., 529, 37-41 (1932).
35. Heuser, R. V., U. S. Patent 1,588,731. *C.A.*, **20**, 2565 (1926).

36. Hill, H., *Journal and Proc., Inst. Sewage Purif., Part I*, 161-6 (1947).
37. Hoover, C. R., and Masselli, J. W., *Ind. Eng. Chem.*, **33**, 131-4 (1941).
38. Hubbs, C. L., "The Toxicity to Fish Life of Cyanide Solutions," Report No. 207, Institute for Fisheries Research, University of Michigan. Cited by Eldridge, E. F., Ref. 21.
39. Ref. 30, pp. 81-191
40. Jenkins, S. H., and Hewitt, C. H., *J. Soc. Chem. Ind. Trans.*, **59**, 41-4 (1940).
41. Kelch, J. L., and Graham, A. K., *Plating*, **36**, 1208-31 (1949)
42. Klassen, C. W., Hasfurther, W. A., and Young, M. K., *Proc. 4th Ind. Wastes Conf., Purdue Univ.*, 229-37 (1949).
43. Kneale, J. B., and Lucas, C. D., Thesis, Case Inst. Tech. (1950). Cited by Rudolfs, W., *et al.*, *Sewage and Ind. Wastes*, **22**, 1162 (1950)
44. Leighton, F., Jr., Master's Thesis, Wesleyan Univ., June 1947.
45. Losson, F. J., Jr., and Bloodgood, D. E., *Proc 4th Ind. Waste Conf., Purdue Univ.*, 314-26 (1949).
46. Masselli, J. W., Master's Thesis, Wesleyan Univ., June 1941.
47. McKee, R. H., and Leo, S. T., *Ind. Eng. Chem.*, **12**, 16-26 (1920). McKee, R. H., U.S. Patent 1,408,618 (1922); *C.A.*, **16**, 1541 (1922). Mitter, G. C., and Dighe, S. G., *J. Sci. Ind. Research*, **2**, 11-16 (1943); *C.A.*, **38**, 3911 (1944). Sierp, F., *Vom Wasser*, **14**, 230-51 (1939-40); *C.A.*, **35**, 4890 (1941). Sierp, F., and Frunsemeier, F., *ibid.*, **15**, 239-57 (1941-2); *C.A.*, **38**, 5626 (1944). Southgate, B. A., and Grindley, J., *Ind. Chemist.*, **21**, 144-52 (1945). Hurd, F. W., U.S. Patent 2,415,950 (1947); *C.A.*, **41**, 2342 (1947).
48. Meinck, F., *Metallwaren Ind. u. Galvano-Tech.*, **40**, 225-29 (1942); *C.A.*, **38**, 3552 (1944). Barnes, G. E., *Water and Sewage Works*, **94**, 8, August 1947. Haseltine, T. R., *ibid.*, **94**, 187-91 (1947).
49. Milne, D., *Sewage and Ind. Wastes*, **22**, 1192-99 (1950).
50. Moir, J., and Gray, J., *J. Chem. Met. Soc. S. Africa*, **11**, 152-6 (1910).
51. Moir, J., and Gray, J., *J. Chem. Met. Soc. S. Africa*, **10**, 133-49 (1909).
52. Morrissey, R. A., cited by Dobson, J. G., *Sewage Works J.*, **19**, 1016-7 (1947).
53. Nesmejanov, *Gesundh.-Ing.*, **58**, 471-76 (1935).
54. Newton, L., *Ann. Applied Biol.*, **31**, 1-11 (1914)
55. Nolte, E., and Bandt, H. J., *Beitr. Wasser-, Abwasser-, u. Fischereichem. Madgeburg*, 1916, 9-14; *Chem. Zentr.* 1947, I, 549; *C.A.*, **43**, 336B (1949).
56. Oeming, L. F., *Sewage Works J.*, **18**, 678-85 (1946).
57. Oyler, R. W., *Plating*, **36**, 341-2 (1949). Sperry, L. B., and Caldwell, M. R., *ibid.*, 343-7 (1949). Oyler, R. W., *Proc. 4th Ind. Waste Conf., Purdue Univ.*, 250-1 (1949).
58. Pearce, L., *et al.*, *Sewage Works J.*, **14**, 53 (1942).
59. Penny, C., and Adams, C., Fourth Rep't., Royal Comm. on Poll. of Rivers in Scotland, **2**, 377-91 (1863).
60. Pettett, E. V., and Thomas, H. M., *Chem. Age (London)*, **59**, 779 (1945).
61. Powers, E. B., *Illinois Biol. Mono.*, **4**, 127-93 (1917).
62. Price, C. C., Larson, T. E., Beck, K. M., Harrington, F. C., Smith, L. C., and Stephanoff, I., *J. Am. Chem. Soc.*, **69**, 1640-44 (1947).
63. Reed, A., *Sewage and Ind. Wastes*, **22**, 1338-42 (1950).
64. "Report of the Water Pollution Research Board, 1939-1945," pp. 49-52, Dept. of Scientific and Ind. Research, His Majesty's Stationery Office, London, 1947.
65. "Report of the Water Pollution Research Board, 1948," pp. 41-48, Dept. of Scientific and Ind. Research, His Majesty's Stationery Office, London, 1949.

66. "Report of the Water Pollution Research Board, 1939-1945," p. 52, Dept. of Scientific and Industrial Research, His Majesty's Stationery Office, London, 1947.
67. "Report of the Water Pollution Research Board, 1932," pp. 31-32, Dept. of Scientific and Industrial Research, His Majesty's Stationery Office, London, 1933.
68. Ridenour, G. M., Backus, R. D., and Sherron, C., *Sewage Works J.*, **17**, 966-78 (1945).
69. Ridenour, G. M., and Greenbank, J., *Sewage Works J.*, **16**, 771-88 (1944).
70. Rudgal, H. T., *ibid.*, **13**, 1218-50 (1941).
71. Rudolfs, W., *Sewage Works J.*, **9**, 728-12 (1937).
72. Rudolfs, W., *et al.*, *Sewage and Ind. Wastes*, **22**, 1157-91 (1950).
73. Rudolfs, W., *Sewage Works J.*, **15**, 48-54 (1943).
74. Schaut, G. G., *J. Am. Water Works Assoc.*, **31**, 771-822 (1939).
75. Schulenberg, W., and Beier, H., German Patent 707,850 (1941); *Chem. Zentr.*, 1941, II, 2,600. Beier, H., German Patent 742,074 (1943); *Chem. Zentr.*, 1941, I, 1209. Beier, H., German Patent 745,311 (1943); *Chem. Zentr.*, 1944, II, 476. Chemische Fabrik Petunia G.m.b.H., Belgian Patent 447,088 (1942); *C.A.*, **39**, 1006 (1945). Meinek, F., *Metallwaren Ind. Galvano-Tech.*, **40**, 225-9 (1942); *C.A.*, **38**, 3552 (1944).
76. Spencer, J. H., *J. Proc. Inst. Sewage Purif.*, 1939, I, 17-38. Abstracted in *Sewage Works J.*, **11**, 920-1 (1939).
77. Sussman, S., Nachod, F. C., and Wood, W., *Ind. Eng. Chem.*, **37**, 618-24 (1945).
78. Unwin, H. D., *Sewage Works J.*, **21**, 501-9 (1949).
79. Waite, C. F., Proc. 5th Ind. Wastes Conf., Purdue Univ., 223-31 (1950).
80. Washburn, G. N., *Sewage Works J.*, **20**, 1071-83 (1948).
81. Wernlund, C. J., and Zunnick, M. J., U.S. Patent 2,191,438 (1940); *C.A.*, **34**, 4675 (1940).
82. White, H. A., *J. Chem. Met. Soc. S. Africa*, **10**, 442-9 (1909); **11**, 15-16, 77 (1910).
83. Williams, R., Jr., *Chem. Eng.*, **56**, No. 9, 96-8 (1949). Gipson, A. H., *Eng. News-Record*, **143**, No. 20, 44-5 (1949). Kessler, R. L., and Oyler, R. W., Proc. 4th Ind. Waste Conf., Purdue Univ., 244-9 (1949). Simpson, R. W., and Thompson, K., *Sewage and Ind. Waste Eng.*, **21**, 302-1 (1950). Tarman, J. E., and Priester, M. U., Proc. 5th Ind. Wastes Conf., Purdue Univ., 40-52 (1950); *Water and Sewage Works*, **97**, 385-9 (1950). Milne D., Uhl, P. W., Roy, E. J., and Hauri, C. F., *Sewage and Ind. Wastes*, **23**, 64-81 (1951).
84. Wischmeyer, W. J., and Chapman, J. T., *ibid.*, **19**, 790-5 (1947).
85. Wise, W. S., Dodge, B. F., and Bliss, H., *Ind. Eng. Chem.*, **39**, 632-6 (1947). Dodge, B. F., Biennial Rep't. State Water Comm. Connecticut, **5**, 51-59 (1934); **6**, 69-77 (1936); **8**, 59-68 (1940). Bliss, H., and Dodge, B. F., *ibid.*, **9**, 48-58 (1942).
86. Wise, W. S., *Sewage Works J.*, **20**, 96-102 (1948).
87. Wittmann, O., and Wohlfahrt, R., *Chem.-Ztg.*, **61**, 496 (1937).
88. Woelfle, A. H., *Sewage Works J.*, **14**, 402-3 (1942).

14. Waste Disposal Problems in the Mining, Preparation, and Carbonization of Coal

Willard W. Hodge

Mellon Institute, Pittsburgh, Pa.; Senior Fellow on the Effluents Treatments Fellowship of Koppers Company, Inc.

Introduction

The developments which have afforded humanity the annual production and utilization of millions of tons of coals—anthracite, bituminous, and lignite—are among the outstanding achievements of our industrial civilization during the past two hundred years. The existence of coal in the earth's strata has been known for more than two thousand years and evidence indicates that some minor uses of "coal-like substances" had been made during early times and in different countries.

The first mention of coal in the literature is believed to be that made in the fourth century B.C., by Aristotle in his treatise on Meteorology wherein he wrote: "Those bodies which have more of earth than of smoke are called coal-like bodies." One of his pupils, Theophrastus (about 372 to 287 B.C.) in his book, "On Stones," referred to "Those fossil-like substances that are called coals, which kindle and burn like wood-coals." He and Pliny stated these substances were used by the smiths, and "were found in Lyguria and in Ellis, on the way to Olympias, over in the mountains." The substances were probably brown coals obtained from Thraee in northern Greece and from Lyguria in northwestern Italy. Coal cinders found among the ruins of Roman towns, villas and forts, and especially in Northumberland along the Roman Wall near where coal seams outcrop, indicate that the Romans during their occupation of Britain (about 45 to 350 A.D.) made use of coal for heating purposes. Quite generally accepted as the first written record on the use of coal in Great Britain is a rental lease made in 852 A.D. and recorded in the Saxon Chronicle of the Abbey of Peterborough. By this contract the Abbot of Ceobred let the land of Sampringham to Wulfred, conditioned on his sending to the monastery each year, "Sixty loads of wood, 12 loads of coal, 6 loads of peat" and some other materials. In the descriptions of some of his many

journeys through Asiatic countries, Marco Polo (about 1250 to 1324 A.D.) mentions that the Chinese at a very early date used as a fuel a black, mineral-like stone, similar to coal. Apparently wood and charcoal were the preferred fuels of the early peoples for centuries before there was much utilization of coal.^{6-8,6-13}

The mining of coal assumed industrial importance in England in the 13th century. The invention and development of the steam engine, which provided the power to hoist large quantities of coal from the pits, and also increased the requirements for fuel, for that and other power purposes, greatly accelerated the growth of the coal mining industry. It was retarded by various legal obstacles; as late as the 17th century many cities in Europe objected to the use of coal because of the resulting disagreeable smoke and dust. Some cities had regulations against its use, and during the reign of Henry II of France the smiths were required to have a license or paid fines for using coal in Paris.⁶⁻¹ Perhaps these were the forerunners of the anti-smoke or anti-atmospheric pollution ordinances in force today in many municipalities. However, the requirements for human comfort, especially in the Temperate and Arctic Zones, and the ever increasing demands for transportation, power, construction operations, metallurgical, chemical and other manufactured products have resulted in a rapid and very large, nearly world-wide, development of the coal mining industry.

The world-wide production of coal based on available statistics and estimates for some countries for which there were no reliable data is presented in Table 1. Often the outputs from small, or so-called "wagon-mines," and "boot-leg" coal are not included in national or state statistics.

TABLE 1. WORLD'S COAL PRODUCTION
(In thousands of long tons; 1 long ton = 2,240 lbs, avoirdupois)

Continent	1913	1926	1932	1936	1946*
Africa	8,300	14,000	10,272	15,701	24,500
North America	531,600	607,660	332,165	458,410	545,900
South America	1,600	2,000	1,792	2,790	3,792
Asia	55,000	80,000	79,748	96,173	55,200
Europe	730,000	621,000	662,811	836,849	597,000
Oceania	15,000	16,450	15,707	19,811	16,655
Total	1,341,500	1,341,310	1,102,495	1,428,907	1,243,047

*The first post-World War II year for which fairly complete statistics are available, but no data were given for U.S.S.R., which was one of the large prewar producers. During 1942, the world's production of coal, so far as statistics are available, was approximately 2,071,300,000 net tons, including 355,300,000 tons of lignite, largely from mines in continental Europe. The mining of coal in several important European countries was seriously disrupted by World War II.

Reserves

The types of coal mined are anthracite; bituminous, of which there are several classes; and lignite, brown and black. The principal methods of extracting the coal from the earth are by shaft, drift and slope mines, and open-pit or strip mining. The estimated extent of the world's coal reserves, based on the following assumptions: minimum thickness of workable seams, 1 foot to a depth of 4,000 feet, and seams 2 feet in thickness to depths of 4,000 to 6,000 feet, are given in Table 2. The limit of workable depth was considered to be 6,000 feet.

TABLE 2. WORLD'S COAL RESERVES⁴¹

(In millions of metric tons; 1 metric ton = 2,204.6 lbs, avoirdupois)

Continent	Anthracites Including Dry Steam Coals	Bituminous Coal	Sub-bituminous Coals, Lignite or Brown Coals	Total in Millions of Metric Tons
Africa	11,662	45,123	1,054	57,839
America	22,542	2,271,080	2,811,906	5,105,528
Asia	407,637	760,098	111,851	1,279,586
Europe	54,346	693,162	36,682	784,190
Oceania	659	133,481	36,270	170,410
Total	496,846	3,902,944	2,997,763	7,397,553

Coal Resources of the World. Twelfth International Geological Congress, Toronto, Canada (1913).

A more recent estimate of the world coal reserves, as given by Zimmerman^{G-26} is as follows:

WORLD COAL RESERVES BY CONTINENTS * G-26
(In billions of metric tons)

Continent	Bituminous and Anthracite Coals		Lignite and Brown Coals		Total
	Proved	Probable	Proved	Probable	
North America	30.3	2,286.4	391.3	1,441.4	1,149.1
Europe	548.4	1,561.8	60.1	270.6	2,440.9
Asia	10.9	1,155.5 ^a	0.1	1.1	1,167.6
Africa	9.3	209.7	...	11.9	230.9
Australia	21.4	140.8	10.7	0.6	173.5
Central and South America	2.1	1.1	3.2
	622.4	5,355.3	462.2	1,725.6	8,165.5

* Courtesy, World Resources and Industries (1951).

^aThe figure for Asia has been reduced by 9 trillion.

Many other estimates of world coal reserves have been made and there are wide differences in the quantities estimated. However, all of the estimates indicate, according to present rates of consumption, that humanity will have sufficient amounts of coal to last for several hundred years.

Growth of the Coal Mining Industry in North America

In North America the first discovery of bituminous coal, so far as known, was on Cape Briton Island, Canada, in 1672, and in the United States in 1673. In the record of his journeys, Father Joliet made a note in May 1673 or 1674 of the appearance of "charbon de terra" in the area of what is now the State of Illinois. On a map of the Upper Potomac River country made by Benjamin Wilson, he notes two "cole mines" above the mouth of the Savage River. Anthracite was discovered in Pennsylvania about 1762. The mining of bituminous coal was started on a small scale in Virginia in 1730 and by the French near Louisburg, Cape Breton, in 1740. The first Lehigh Coal Mining Company was formed in 1793 and mining of anthracite is said to have begun in 1807. This coal began to receive recognition in the Philadelphia market about 1812. The first production data recorded for the United States were the shipment of 22 tons of anthracite in 1814 and of 3,000 tons of bituminous coal in 1820. Annual production in the United States of more than one million tons was attained for anthracite in 1837 and for bituminous coal in 1840. From these small beginnings the mining of coal in this country had increased to approximately 574,949,017 tons of bituminous coal, 2,668,310 tons of lignite, and 54,933,909 tons of anthracite in 1945.* The approximate total value of the coal mined in the United States during 1945 was \$2,088,981,764 divided about as follows: bituminous coal, \$1,724,847,051; lignite, \$40,024,650; and anthracite, \$324,110,063. The production data show an all time peak production of bituminous coal and lignite amounting to 630,623,722 tons in 1947, and of 99,611,811 tons of anthracite in 1917. The losses in production of coal during 1945 were not due to any decline in demand for coal, but were due largely to "strikes" by the coal miners' unions. The U.S. Bureau of Labor Statistics show there were 598 strikes in the soft-coal mines that year, with 581,000 workers involved, a loss of 5,007,000 man-days and of the production of 30,000,000 tons of coal; and the hard-coal mines were shut down completely by labor disturbances for three weeks, which meant a loss of production of about 3,500,000 tons of anthracite. Specific production data for the United States are given for several selected years for bituminous coal and lignite in Table 3, and for anthracite in Table 4.²²⁵

The net tons of bituminous coal and lignite produced per man per day employed were: 2.56 in 1890; 3.91 in 1915; 5.78 in 1945; and 6.26 in 1948. The per cent of underground coal production cut by machines was 24.9 in 1900 and 90.7 in 1948. The per cent of total production mechanically cleaned in 1910 was 3.8 and in 1948 was 30.2. The per cent of the total coal

*These data do not include coal from many small (wagon) mines which produce less than 1,000 net tons per year.

TABLE 3. GROWTH OF THE BITUMINOUS COAL AND LIGNITE MINING INDUSTRY IN THE UNITED STATES FROM 1890 TO 1948²²⁵

Year	Production (Net tons)	Total Value (1)	Men Employed	Number of Mines	Number of Strip Pits	Production from Strip Mines (1,000 net tons)	Strip Coal, % of Total
1890	111,302,322	\$ 110,420,801	192,204	(2)	(2)
1895	135,118,193	115,779,771	239,962	2,555	(2)
1900	212,316,112	220,930,313	304,375	(2)	(2)
1905	315,062,785	334,658,294	460,629	5,060	(2)
1910	417,111,142	469,281,719	555,533	5,818	(2)
1915	442,624,426	502,037,688	557,456	5,502	60 (5)	2,832	0.6
1920	586,666,683	2,129,933,000	639,547	8,921	174 (5)	8,860	1.5
1925	520,052,741	1,060,402,000	588,493	7,144	227	16,871	3.2
1930	467,526,299	795,483,000	493,202	5,891	218	19,842	4.3
1935	372,373,122	658,063,000	462,403	6,315	368	23,647	6.4
1940	460,771,500	879,327,227	439,075	6,324	638	43,167	9.4
1944	619,576,240	1,810,900,542	393,347	6,928	1,240	100,898	16.3
1945	577,617,327	1,768,204,320	383,100 (4)	7,033	1,370	109,987	19.0
1947	630,623,722 (3)	2,622,634,946	419,182 (4)	8,700	1,750	139,395	22.1
1948	599,518,229	2,993,153,747	411,631 (4)	9,079	1,971	139,506	23.3

(1) Figures on value for 1890 to 1935 inclusive exclude selling expense, but it is included for the other years.

(2) Data not available.

(3) All-time record annual production.

(4) Average number of men working daily.

(5) Exclusive of horse stripping operations.

production mined by stripping was 0.6 in 1915; 4.3 in 1930; 9.4 in 1940; and 19.0 in 1945. The approximate number of strip mines in 1930 was 218; in 1940, 638; and in 1945, 1,370. The coal produced from strip mines in 1940 was 43,167,000 tons and in 1945 it was 109,987,000 tons. The average amount of coal produced per man per day in 1948 was 15.28 tons from strip mines and 5.31 tons from underground mines.²²⁵ These data show the rapid growth of strip mining during recent years; operations which have created some more problems in the disposal of industrial wastes in addition to those arising from the deep coal mines.

WASTE DISPOSAL PROBLEMS IN THE MINING OF COAL

The wastes from the mining of coal may be divided into three classes: solid, liquid, and gaseous. The solid wastes come from the over-burden of the coal seam and from the opening of the mine. They include earth, rock and shale and a certain amount of waste coal. Also in mining the coal a certain amount of these wastes may occur in the seam, especially if faults are encountered in removing the coal. The liquid wastes include

TABLE 4. PRODUCTION STATISTICS IN THE PENNSYLVANIA ANTHRACITE INDUSTRY FROM 1890 TO 1948²²⁵

Year	Production (Net tons)	Total Value	Average No. of Employees	Average Tons per Man per Day	Quantity Cut by Machines (Net tons)	Quantity Produced by Stripping (Net tons)
1890	46,168,611	\$ 66,383,772	126,000	1.85
1895	57,999,337	82,019,272	142,917	2.07
1900	57,367,915	85,757,851	144,206	2.40
1905	77,659,850	141,879,000	165,406	2.18
1910	84,485,236	160,275,302	169,497	2.17
1915	88,995,061	184,653,498	176,552	2.19	1,307,756	1,121,603
1917	99,611,811 (1)	283,650,723	151,174	2.27	1,955,223	2,301,588
1920	89,598,249	434,252,498	145,074	2.28	938,073	2,054,411
1925	61,817,149	327,661,512	160,312	2.12	941,189	1,578,478
1930	69,384,837	354,574,191	150,804	2.21	1,410,123	2,536,288
1935	52,158,783	210,130,565	103,269	2.68	1,848,095	5,187,072
1940	51,484,640	205,489,844	91,313	3.02	1,816,483	6,352,700
1944	63,701,363	354,582,884	77,591	2.79 (2)	1,336,082	10,953,030
1945	54,933,909	323,944,435	72,842	2.79 (2)	1,210,171	10,056,325
1948	57,139,948	467,051,800	76,215	2.81	1,016,757	13,352,874

(1) The maximum annual production of Pennsylvania anthracite.

(2) This figure includes some "bootleg" coal purchased by legitimate operators and prepared at their breakers; this "bootleg" coal is not included in calculations of output per man per day, since data on number of men working to produce the "bootleg" anthracite are not available. Data for net tons anthracite loaded mechanically underground begin in 1927 with 2,223,281 tons and increased gradually to 14,975,146 tons in 1941 and was 13,927,955 in 1945.

surplus water which occurs in large volumes in many mines, especially in the Anthracite Region of Pennsylvania. The water flowing from many of the mines often develops acid properties and is known as acid mine drainage. The gases are emitted from a few coal seams in the bituminous areas in what are known as "gassy" mines. The gas is largely methane although carbon monoxide and carbon dioxide may be present to some extent. No economical method has been developed for capturing the methane, which would make a good fuel if sufficiently concentrated. The presence of the hydrocarbon gases and carbon monoxide in the mine is dangerous since they may form explosive mixtures with air, and the mixture may be ignited by sparks from the electrical equipment or by the lamps or matches carelessly used by the miners. The ventilation of gassy mines therefore is often more costly than for mines of equivalent tonnage from which dangerous gases do not have to be exhausted.

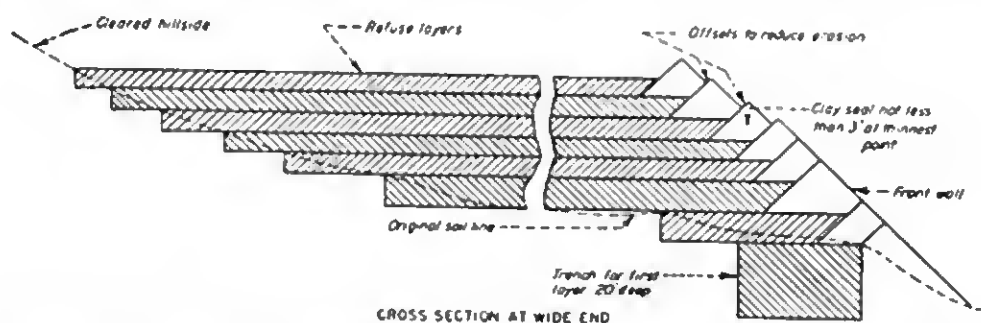
The disposal of the solid materials from mining is usually carried out by simply hauling the materials to a nearby dump, which may be a conveniently located ravine or level area near the mouth of the mine.

Some of these piles of earth, rock, waste coal, sulfur balls and other debris are built up to very large sizes which are often called "gob-piles." Many of these gob-piles are largely composed of inert material and do not cause objectionable stream or air pollution although they may appear rather unsightly. However, many other refuse piles contain sufficient combustible coal and other organic matter that they often take fire spontaneously or ignite accidentally from lighted matches or other sources. Large gob-piles may burn for many months or even years producing considerable volumes of sulfur dioxide, carbon dioxide and smoky fumes, thus causing atmospheric pollution. They also often contain sulfuritic material which oxidizes in moist air forming soluble iron and aluminum sulfates, some of which are hydrolyzed by water and produce an acid run-off during the rains. The occurrences of carbon monoxide in toxic concentrations at ground levels of refuse piles and slightly lower have been reported by Nelson and Hall.¹⁵⁴ At head level during these tests the concentrations of carbon monoxide were not dangerous. Considerable stream pollution is caused by the acid run-off from gob-piles located in some of the very active coal mining areas. After the gob-pile has burned out there remains a brownish-red ash mixed with gray material, and this is spoken of as "red dog." Millions of tons of red dog are used in western Pennsylvania, West Virginia, eastern Ohio, parts of Virginia and Kentucky, as filling for the berms of highways and as surfacing materials on country roads, private driveways and parking lots. This appears to be the only useful by-product obtained from the semi-combustible solid refuse from the coal mines. Millions of tons of the non-combustible waste solids from the mines are used for filling purposes for the operating yards near the entrances of coal mines and for parking areas.

In comparatively recent years methods have been developed for alleviating the objectionable atmospheric pollution which occurs quite often during the burning of the large gob-piles. One method is to convey the waste materials to a continuously burning refuse pile or to some type of outdoor furnace in which the combustible materials are burned as they are discarded from the mine. There is, naturally, some pollution of the air by the sulfur dioxide and fumes caused by combustion of the refuse, but since it burns continuously in small amounts the concentrations of objectionable fumes and gases in any local area seldom become as great as they do when a large gob-pile is burning. One of the active investigations on this problem is being carried out by Nelson and Hall¹⁵⁴ on the Coal Waste Fellowship at Mellon Institute of Industrial Research. The Fellowship is sponsored by the Western Pennsylvania Coal Operators Association and close cooperation is maintained between the laboratory research and its applications at the coal mines operated by members of

the Association. The danger of gob-pile fires is reduced by compacting the refuse in layers.

Two improved methods for disposing of the solid refuse from the mines are now being used. Both involve sealing the piles of refuse so the moisture and oxygen of the air will not have free contact with the combustible material in the gob-pile. For refuse piles which contain relatively large amounts of combustible material a type of sealing with clay is practiced as follows: The layers of refuse are compacted, usually by rolling with a heavy power roller, then a layer of clay is put over the top of the packed



(Courtesy, Coal Waste Fellowship, Mellon Institute; Rochester and Pittsburgh Coal Company)

FIGURE 1. Method of clay-sealing edges of cleaning plant refuse piles

refuse. This is followed by alternate layers of coal mine solid wastes and clay. In addition to these layer applications of clay, the sides or edges of the refuse pile are also sealed with clay. This type of disposal requires large quantities of clay and is probably not necessary for solid mine wastes which contain small amounts of combustibles. Under the latter conditions the gob is packed into successive layers and only the edges are sealed with clay. A diagram of this method of disposal is shown in Figure 1. Both methods are reported to be giving satisfactory results in avoiding gob-pile fires and preventing the acid run-off from the piles. Further investigations are in progress on this Fellowship, and at other institutions.

A method for ameliorating objectionable stream pollution from the rain water run-off of acidic materials from gob-piles has been described by Gross and Lee.⁸³ The method involves construction of an earth dam at a distance from and around the base of the gob-pile, the run-off from the gob-pile is impounded by this dam during periods of low stream flow and the acidic waste water is discharged to the stream during periods of very high river flow. It was reported that this method of safeguarding the stream from excessive acid pollution during periods of low flow has proved quite satisfactory not only to the state officials but also to the property owners located downstream from the mining operations.

Another important solid waste in the mining industry is the coal which

is left underground. It is necessary to leave some of this coal as pillars to support the mine roof and to support buildings and roadways from caving into the mine. However, according to Eavenson,⁶⁶ considerable coal losses underground might be avoided by improved mining methods and good housekeeping. The coal recovery from some mines is only around 60 to 70 per cent of the total coal in the seam. In some mines in southern West Virginia, Salvati¹⁷⁷ states the recovery is around 80 to 90 per cent of the available coal. The recently developed method of supporting mine roofs by bolting them to higher strata is said to afford possibilities of higher percentages of recoveries of the coal in the mines and to facilitate transportation of the coal from within the mine to the tippie, since there will be very few pillars or other obstructions on the floor of the mine.^{177a} By applying modern methods, it has been estimated that from 85 to 95 per cent recovery of coal can be accomplished by efficient management in many of the mines. The loss of the coal left underground is partly necessary and may be partly a waste problem, but the coal left in the mine, especially that known as "fines," "bug dust" and "sulfur mud," is believed to be the source of much of the acid mine drainage which flows or is pumped from abandoned mines or sections of some active mines. The coal mining industry, through Bituminous Coal Research, Inc., and Schools of Mines, sponsors research for developing methods to increase the percentage of recovery of the coal available in the seams.

WASTES FROM THE PREPARATION OF COAL

Anthracite has been mined in Pennsylvania for more than 100 years and this industry has been the leader in the preparation of coal for marketing and for special purposes.⁶⁻¹² The preparation involves a number of different operations depending upon the uses to be made of the coal. The first step in the preparation of many anthracite and bituminous coals is hand picking, which is done by employees placed along a continuously moving conveyor. These employees pick off the pieces of slate, rock, sulfur balls or other undesirable materials in the run-of-mine coal and thus separate the refuse from the good coal. This simple method still prevails, but in most of the collieries in the anthracite region and at many bituminous mines, hand picking is followed by size screening. The fine sizes are then conveyed to coal washeries, some of which have been in operation for many years. The crushed coal is washed with water, often surplus water pumped from the mine, the fines and much of the lighter gravity refuse is washed from the good quality of coal. The types of equipment and conveying systems used for handling the refuse at the anthracite mines have been described and illustrated by Clark.³⁹ He also discusses

the disposal of solid refuse from large size rocks and slate to the finer materials. The fine waste is known as anthracite culm and contains various sized particles of anthracite as well as considerable refuse from the mining and crushing operations. The properties and disposal of anthracite culm and silt have been discussed by Sisler, Fraser and Ashmead,¹⁸⁷ Yancey and Fraser,²³⁶ Parton,¹⁶¹ Hebley⁹³ and others. For many years the fines were discharged into the rivers in the anthracite regions and were the cause of objectionable stream pollution. In 1936, the Corps of Engineers, U.S. Army, estimated the amount of anthracite culm and silt accumulated in the bed of the Schuylkill River, upstream from the Fairmont Dam at Philadelphia, at 24,000,000 cu yds and the annual influx of this material at 650,000 tons. In describing some of these coal washery plants, Parton¹⁶¹ has also referred to the large amount of anthracite culm and silt which has accumulated in the other larger rivers of the Anthracite Region. It has been estimated that in the Northern Field, approximately 13 per cent of the marketable coal has been lost by washing with the older type breaker operations and this figure is believed to be considerably higher in the southern and middle Anthracite Fields. A considerable quantity of the silt in the bottom of some of these rivers has been recovered by dredges mounted on barges. The "river coal" may be screened and excess water drained away and then it is sold for certain purposes. The developments by mechanical and combustion engineers of methods for burning very fine sizes of pulverized coal opened markets for this recovered silt. However, some of the dredged silt contains too much clay and soil to be efficiently used as a fuel. It has been reported that one power plant in Harrisburg, Pa., uses around 250,000 tons of recovered anthracite fines per year. The fines have also found a market in the cement and other industries which utilize pulverized coal. The increased market for fine-sized coal has led to the development of far better cleaning and preparation methods not only in the anthracite but also in the bituminous coal mining industries. Some of the newer preparation plants recover all but the very finest particles of coal and yet separate out quite satisfactorily undesirable refuse. The sulfur and ash content of prepared coal is usually much lower than untreated or run-of-mine coal.

Another feature which has greatly reduced the amount of anthracite fines being discharged to the streams has been the cooperative activity of the Pennsylvania Sanitary Water Board, acting under the Purity of Waters Act passed by the Pennsylvania Legislature in 1937 and further revised in 1945 and 1947. Under this law, mining companies are required to obtain permits for the discharge of waste materials into the waters of the Commonwealth. As originally passed, the law exempted the coal mining

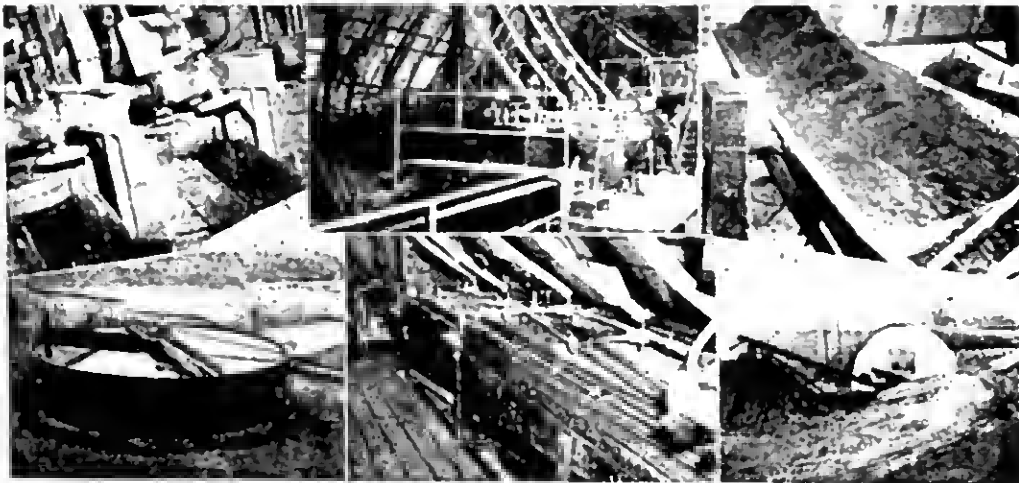
industries. But revisions have brought certain restrictions on coal mining such as the discharge of unnecessary culm or fines into the streams and has placed limits on the amounts of acid mine drainage which may be discharged to certain waterways. The improvements of stream conditions in Pennsylvania have been described by Hoffert^{109,110} and by Siebert.¹⁸⁵ The latest development along these lines has been the large project for cleaning up the Schuylkill River in which the Federal government cooperated with the Commonwealth of Pennsylvania and the anthracite mining industries in dredging millions of tons of accumulated silt from the river, thus reopening this important waterway to deep river transportation. This project involved expenditures of several million dollars and has been described in different issues of *Clean Streams* published by the Pennsylvania Sanitary Water Board, Department of Health.

A large coal preparation plant in the Anthracite Region is shown in Figure 2. The operations applied are crushing and grinding, conveying, screening, and sizing, flotation and/or settling and the final effluent containing very little finely suspended matter is usually discharged to a settling lagoon of size sufficient to give the necessary detention period for even the very fine particles to settle before the supernatant, clarified effluent is discharged to a receiving watercourse. The increased demands for coal of specified properties have led many of the bituminous coal mining companies to construct coal preparation plants. Most of these plants are of the water washery type, but there are also some preparation plants which apply what is known as air cleaning. Very similar general procedures are followed to those in the anthracite coal preparation plants but there are certain differences because of variations in the specific gravities of the coal and of the impurities which occur in the run-of-mine coal. The tailings, or final effluent from the preparation plants, are frequently discharged to a settling lagoon for clarification before the effluent is discharged to the receiving waterway. The preparation plants have been described and discussed by Yanecy and Fraser.²³⁶

A flow diagram of a bituminous coal washery is given in Figure 3, and an illustration of a bituminous coal preparation plant is shown in Figure 4. In this plant, the final waste is disposed of in an impounding lagoon of sufficient capacity to allow the suspended solids to settle out before the clarified effluent overflows the waste weir and is discharged to a receiving waterway. There is considerable research going on at the present time for further improvements in the methods for cleaning and preparing both anthracite and bituminous coal, with the following three objectives: (1) a more careful sizing of the saleable coal, (2) recovery of as much as possible of the worthwhile coal, and (3) the abatement of water pollution.



Concrete clarifier, 120 feet in diameter, under construction at Pine Ridge Colliery of Hudson Coal Co. Unit is now in operation



(Courtesy, "Clean Streams," published by the Pennsylvania Department of Health, Harrisburg, Pa.)

Upper left—Close-up of pumps handling classifier underflow; *Upper center*—Looking toward rear of froth flotation house showing flotation cells in foreground and oil feeding equipment in background; *Upper right*—Dewatering screen conveyor at front of froth flotation house, delivering recovered fine coal to outside storage pile; *Lower left*—Classifier, pumps and screen house—classifier receives mixture of fine coal and silt from breaker, underflow goes to pump house for screening and delivery to froth flotation house—overflow goes to silt pond; *Lower center*—Looking down center aisle toward froth flotation cells; *Lower right*—General view of fine coal removing plant, showing reclaimed fine coal in foreground.

FIGURE 2. Coal preparation plant in the Anthracite Region and the desilting, reclamation system at an anthracite breaker

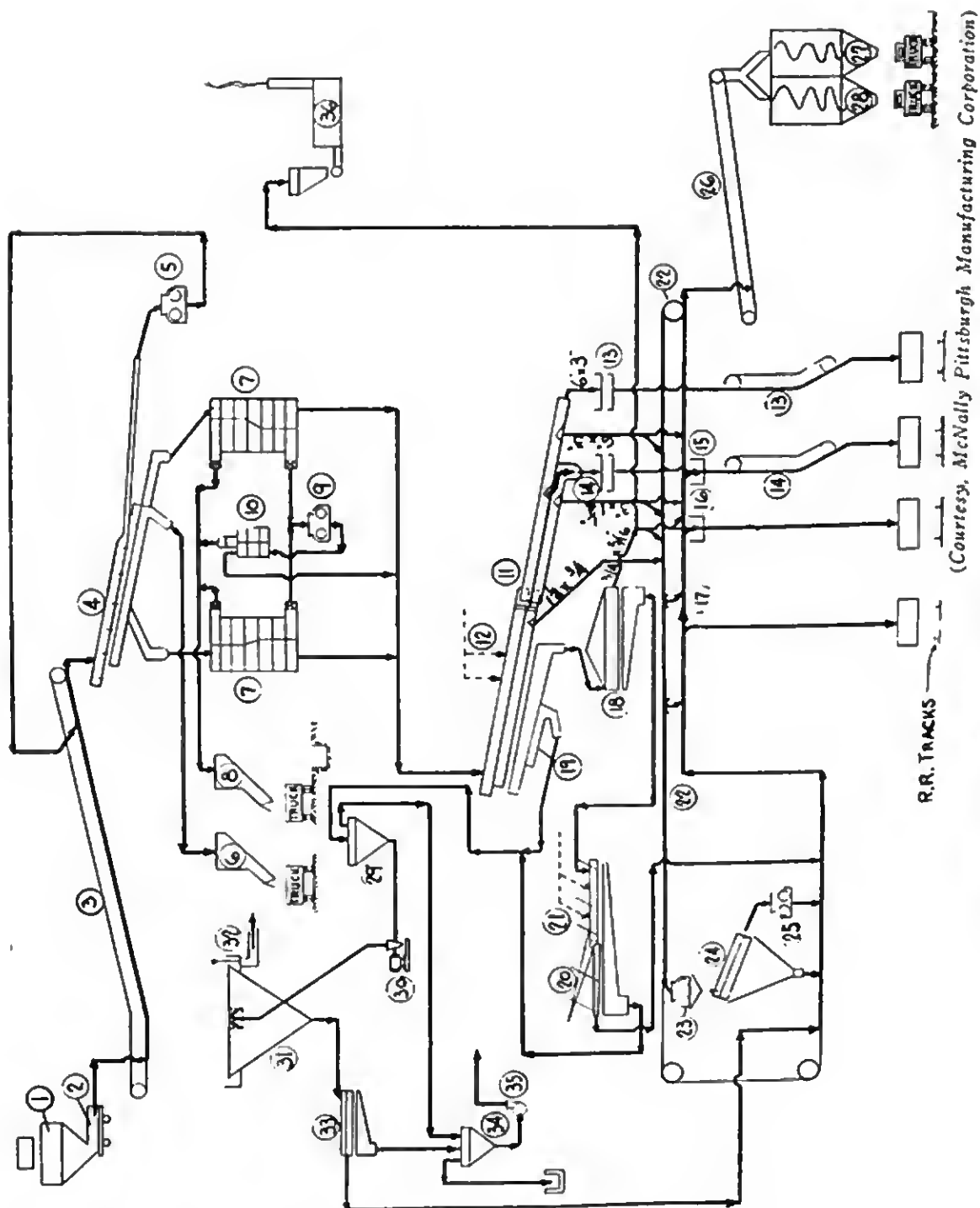


FIGURE 3. Flow diagram of a bituminous coal washery

LEGEND FOR FIGURE 3

FLOW SHEET OF COAL PREPARATION PLANT
INPUT—600 TONS PER HOUR OF STRIP-MINED BITUMINOUS COAL

1. Truck or Railroad Car Dump Hopper, 125 tons capacity, for Run-of-Mine Coal.
2. Reciprocating Feeder, 600 t.p.h. capacity.
3. Run-of-Mine Feed Conveyor.
4. Run-of-Mine Screen and Picking Table for +6" Lump. Making 6" Lump and 6" to 0 feed to two Wash-boxes.
5. Double Roll Crusher breaking +6" coal to 6" to 0 size.
6. Rock Bin for Loading Trucks with +6" Refuse.
7. Two McNally-Norton Wash-boxes, cleaning 6" to 0 raw coal.
8. Refuse Bin for Loading Trucks with 6" to 0 Refuse from the Wash-boxes.
9. Double Roll Crusher breaking 6" to 0 Middlings to 1¼" to 0 before rewashing.
10. McNally-Norton Wash-box, recleaning 1¼" to 0 Middlings.
11. Washed Coal Classifying Screen, separating washed coal into 6" to 3", 3" to 1¼", 1¼" to ¾" sizes and ¾" to 0 and wash water.
12. Fresh Water Sprays.
13. Boom for Loading 6" to 3" coal into railroad cars.
14. Boom for Loading 6" to 1¼" or 3" to 1¼" coal, into railroad cars.
15. Gate and Chute with Flop Gate for Loading 3" to 0 coal into railroad cars.
16. Gate and Chute with Flop Gate for Loading ¾" to 5/16", 1¼" to 5/16" or 1¼" to 0 coal into railroad cars.
17. Gate and Chute with Flop Gate for Loading 1¼" to 0 coal into railroad cars.
18. Vibrating Screens making ¾" to 5/16" coal and —5/16" coal with water.
19. ½ millimeter Wedge Wire Screen.
20. Dewatering Screens making 5/16" to ½ mm coal.
21. Fresh Water Sprays.
22. Two-Compartment Mixing Conveyor.
23. Double Roll Crusher breaking 6" to 1¼" coal to about 2" to 0.
24. Vibrating Screen making 1¼" separation.
25. Double Roll Crusher making 1¼" to 0.
26. Conveyor delivering 6" to 1¼", 3" to 1¼" and ¾" to 5/16" to two 50 ton Truck Loading Bins.
27. Truck Loading Bin for 6" to 1¼" or 3" to 1¼" coal.
28. Truck Loading Bin for ¾" to 5/16" coal.
29. Recirculating Water Sump.
30. Recirculating Water Pump.
31. Overhead Settling Cone.
32. Clarified Water by Gravity to the Wash-boxes 7 and 10.
33. Vibrating Screen recovering plus ¼ millimeter coal.
34. Slurry Waste Sump.
35. Slurry Pump delivering to Slurry Pond, Capacity 550 g.p.m.
36. Heating Plant for Coal Preparation Plant.



FIGURE 4. Refuse disposal by belt conveyor at a coal preparation plant in the hills of West Virginia

COAL MINE WATERS—ACID MINE DRAINAGE

The removal of large volumes of water is a problem common to most anthracite and many bituminous coal mines in the United States, but there are some relatively dry mines. The mine water flows by gravity from some coal mines, but from many mines the water has to be pumped to the surface where it may be discharged directly to a watercourse or part of it may be utilized in washeries for cleaning coal, or if of satisfactory quality a portion of it may be applied as cooling water in condensers or other plant equipment before reaching a receiving waterway. The water from some mines is slightly alkaline or neutral, but that from many anthracite and most bituminous coal mines in certain districts in the United States becomes acid in reaction, usually within a few months after the beginning of mining operations. The disposal of liquid wastes from coal mines in Europe has not been so serious a problem, and according to Bach¹⁶ there is comparatively little acidic mine water from the coal mines of Germany. In France, as stated by Crichton,⁵¹ the mines do not produce acid drainage, probably because there is an overlying bed of chalk which extends from the surface to a depth of about 300 feet. In Great Britain, the mines are usually deep, ranging from 1,000 to 4,000 feet, and they have comparatively little water. In some mines water must

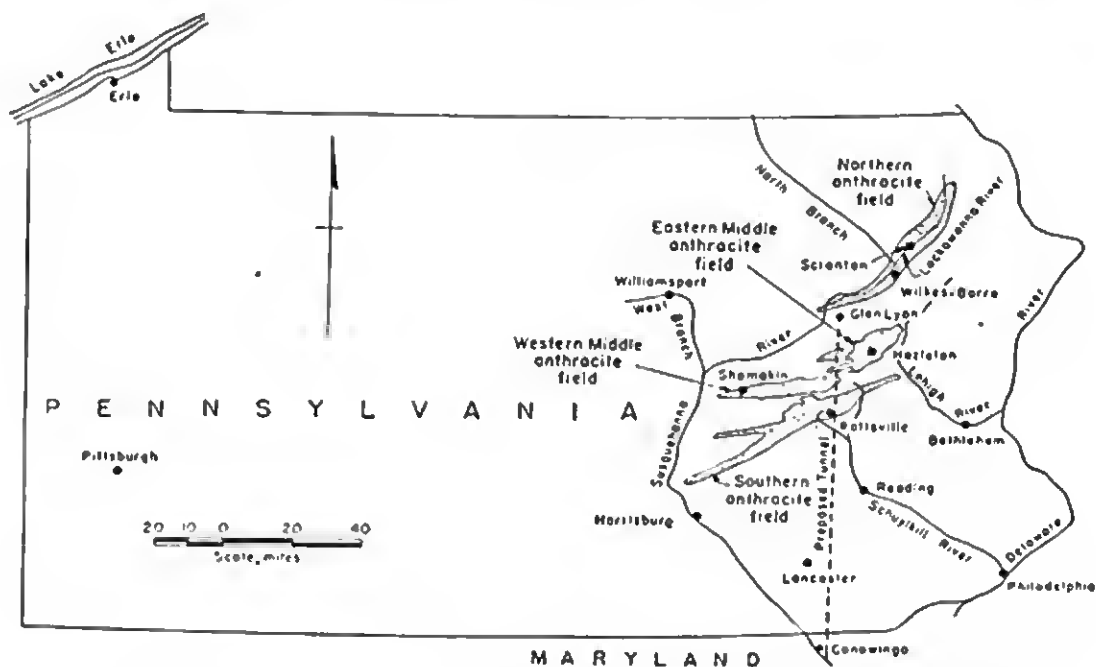
be carried underground to lay the dust. The mines do not produce much acid water, perhaps because the coal is low in sulfur and often the coal seams are in contact with limestone. However, according to Southgate⁶⁻¹⁹ the waters from some mines cause red deposits of iron oxide in the receiving waterways. At some collieries the mine drainage is of sufficiently good quality to be used as boiler water, and in Yorkshire the water from some mines is used for domestic purposes.

The large volumes of water resulting from the very necessary mining of coal can be looked upon quite largely as a waste disposal problem which has marked effects on the flow and quality of the receiving stream. In several cases the costs for pumping out the mine water have become so high that mining operations have necessarily ceased and the mines have been allowed to flood. The sources of water in coal mines are from surface seepage, water flowing into the mines through breaks in the mine roofs or faults or fractures in the strata, underground springs or water tables, and in a few places, brines in the regions of salt wells or near the coasts or extending out under the ocean where there may be seepage of salt water into the coal mines. However, most under-sea mine workings are relatively dry.

Water Disposal Problems in the Anthracite Mines

The disposal of very large volumes of surplus water from the anthracite mines, according to Ash,² has been a very serious problem for many years. The Pennsylvania Anthracite Mining Region comprises about 480 sq miles, and is the largest such area in the world. The region extends from the Delaware River to the Susquehanna River, and these streams with their major tributaries, the Lehigh, Schuylkill, and Lackawanna Rivers, provide the principal natural drainage for the Anthracite Region (Figure 5). With the extended development of anthracite mining these rivers have not carried away sufficiently rapidly the great volumes of water from the mines; also the water in some of the mines is below the level of the rivers. Hence, in many anthracite mines large pools of water have accumulated and in certain sections constitute a potential hazard to life and property. An extensive investigation of the pools in deep mines and strip mines was conducted by Ash⁴ and associates of the U.S. Bureau of Mines. They studied conditions in all four anthracite fields, Northern, Eastern and Western Middle, and Southern, and classified the pools in five types depending on the quantities of anthracite reserves which could be recovered if the pools could be economically dewatered. They also described the kinds of barriers which should be constructed if the inundated areas were dewatered, or to keep the waters safely impounded. The acidity of the pools was investigated along with other properties of the waters.

No data were obtained for hundreds of small underground pools. The information assembled established the following conclusions: More than 200 billion gallons of water are removed annually from the mines in the Anthracite Region by pumping and through drainage tunnels. In 159 pools in underground mine workings, about 91 billion gallons of water are impounded which is not tributary to present drainage systems. In 141 pools in abandoned strip mines, some 2.3 billion gallons of water are



(Courtesy, U.S. Bureau of Mines Bulletin 513, 1952)

FIGURE 5. Line of proposed main drainage tunnel from Conowingo, Md., to Glen Lyon, Pa.

impounded. Many of the pools constitute hazards to future mining operations, especially if there should be serious interference with present pumping operations. Under some of the pools there were no appreciable coal reserves; in other places, considerable quantities of valuable anthracite have been inundated and are lost to production unless a low cost method for dewatering the pools can be developed.

The number of partially flooded and flooded areas in the Anthracite Region has increased from two in 1932, to eleven in 1938, to fourteen in 1941, to twenty-six in 1944. The abandonment of collieries in the Southern Anthracite Field during the period 1923 to 1940 resulted in the flooding of approximately 60 sq miles, about 30 per cent of the field, and this caused additional pumping costs to many of the mines that continued to operate. During 1935 the rainfall in mine inspection District No. 7 of the Southern Field was 92,083,000,000 gal and the total water pumped from

the mines was 36,274,000,000 gal of which 23,124,000,000 gal was pumped from idle mines and 13,150,000,000 gal from operating mines. These mines produced 3,236,575 net tons of coal or a ratio of 46.68 tons of water pumped per ton of coal produced. In the Northern Field, as reported by Lutz and Griffith,¹³⁸ during the last six months of 1942, the rainfall was 26.06 inches, only 4.35 inches more than the average for this District during an equivalent time period. Of the 80,559,444 tons of rainfall during this period on the approximately 46.2 sq miles of the area tributary to the anthracite mines pumping plants, some 72,687,661 tons went underground, an inflow of 88 per cent compared to a 64 per cent inflow and 36 per cent run-off during normal conditions in a normal region. During this period the Hudson Coal Company had to handle 38.8 tons of water per ton of coal mined and one half of the total energy generated and purchased (44,322,980-kw. hours) was required to pump out the water sufficiently so that coal could be mined at a time when it was greatly needed. According to Griffith,⁸² another of the large coal companies in the Northern Anthracite Field reported the following increasing ratio of tons of water pumped per ton of coal produced underground: 8.4:1 in 1920; 11.4:1 in 1930; 26.2:1 in 1935; 32.7:1 in 1940; and 30.3:1 in 1942. In the northern field there are 26 water pools estimated to contain 11,926,482,000 gal of stored water. The overflow elevation of each pool is of importance to mining operations at lower levels

Since pumping very large volumes of water from the mines is necessary in most anthracite and many bituminous coal mines, the types of pumps installed and costs for their operation are important economic factors. The types of pumps used range all the way from the air or steam-driven single piston pumps installed as early as 1868 to electric motor-driven vertical quintuplex and horizontal triplex pumps installed in some anthracite mines from 1917 to 1920. The first general use of centrifugal pumps was about 1906, and since then installations of electrically driven centrifugal pumps have gradually replaced the older types of pumping equipment. In recent years deep-well and shaft types of pumps have been installed. These have been described by Lesser.^{134a} In the comprehensive compilation of data on "Pumping at the Anthracite Mines of Pennsylvania," Ash and associates⁶ have classified the pumps used, as follows: centrifugal—horizontal, vertical, standard, deep-well, and shaft; and displacement pumps—plunger, piston, and shaft. Illustrations are given of installations of the different types of pumps and their comparative advantages are discussed.

Other methods for controlling the water levels in the mines are drainage tunnels and diversion of surface water from flowing into the mines. Drainage tunnels are applicable where the coal mines are located at

elevations higher than those of the natural drainage horizon of the surrounding surface. There are several drainage tunnels in the anthracite region, mainly in the Middle Anthracite Field. The very large Jeddo Tunnel in the Eastern Middle Field is comprised of the parent tunnel, which is about 15,000 ft in length, and four tributary branch tunnels having a total length of 27,787 ft. The cost of construction adjusted to present day values is estimated at more than \$3,000,000. In 1943 the collieries which contributed their water to this tunnel system produced 1,791,637 net tons of anthracite from underground mining and handled 24.3 tons of water per ton of this coal. Of this amount of water, 4.5 tons were pumped to the surface for use in the preparation of the coal and 19.8 tons flowed through the tunnel drainage system. Where the topography for drainage tunnels is favorable, the high initial cost for construction and relatively low maintenance cost for a drainage tunnel should be compared with the costs for pumps, pipes, power and maintenance of a pumping system for freeing the mine of surplus or waste water.

For the diversion or control of surface waters, small to large earthen ditches, sometimes lined with open tile or concrete to prevent seepage into the mine, are dug and collect the surface run-off waters to conduits or flumes, usually constructed of creosoted wood. During critical times the large volumes of collected waters flow through these ditches to a watercourse and are thus kept out of the mines. The wooden flumes are usually of the square box or semi-circular type and range from about 36 to 96 inches in width. The Glen Alden Coal Company in its Wyoming Valley, Pennsylvania, workings maintains more than 10,000 ft of wooden flumes and several miles of paved or earthen ditches to divert surface water from flowing through vein crops and broken ground into the underground coal workings. The Warrior Run flume is the longest in this installation, being 3,200 ft long and 90 inches wide. This company and several other companies have quite similar installations at different workings for diversion of surface water. In addition to having to combat these general surplus water conditions, several companies have had to undertake long and expensive dewatering operations caused by flooding of the mines during inactive periods, or to remove danger of drownouts by water impounded in adjacent abandoned mines. Large bodies of dammed-up water may constitute a potential danger to human life and property, hence precautions, often quite costly, have to be taken by the coal companies to avoid sudden collapse of barriers with resulting inundation of active workings or catastrophies to workmen and properties.

In addition to the millions of dollars spent annually to pump water from mines, deflect it into drainage tunnels, and divert surface water

from entry into the mines, there are millions of tons of coal lost irrevocably in protective pillars and in areas reserved under rivers, creeks, swamps, and "buried valleys" in order to protect life and property from sudden floods, intrushes of water due to floods, or breaks in the surface strata. There has been an increase of about 200 per cent during the past twenty years in the quantity of water pumped from underground anthracite mining operations and in the costs for handling the surplus water. The costs under present conditions for handling anthracite mine drainage, including underground pumping, drainage tunnels, and diverting of surface waters, are estimated as about \$10,000,000 per year.⁸² The great and continuing increases in the quantities of water that must be handled threaten the anthracite industries with large reduction in operations and premature extinction unless a broad cooperative remedial program is soon undertaken.

Several plans have been proposed to solve the surplus mine water problem of the Anthracite Region. A plan which is currently attracting wide interest and serious consideration is the construction of a proposed mine water drainage tunnel to serve the entire Anthracite Region of Pennsylvania. The United States Bureau of Mines has sponsored extensive topographical, geological, mineralogical, and chemical field surveys and laboratory investigations on this proposed drainage tunnel. Ash and associates of the United States Bureau of Mines^{6a} have described the sites where fifteen core-drilling operations have been completed. They have discussed at some length the results obtained. The costs of such a tunnel would be too large for the anthracite industry to finance. One estimate placed the cost of the 100-mile tunnel at \$175,000,000. If it is undertaken it would be as a cooperative project by the Federal Government, the Commonwealth of Pennsylvania, and the anthracite industry. It is believed that a satisfactory hydraulic gradient is available. The proposed tunnel appears to have many advantages, but there are many technical and economic factors still to be considered. The line of the proposed tunnel is shown in Figure 5. It would extend from Glen Lyon, Pennsylvania, south to Conowingo, Maryland, where the mine water would be discharged into the Susquehanna River immediately downstream from the Conowingo Dam. The project is receiving further consideration, and the several factors are being evaluated.

Surplus Water in the Bituminous Coal Fields

Many of the bituminous coal mining companies have problems in the disposal of excess water from the mines. However, on the average the disposal of surplus water is not as great a problem in the bituminous fields as it is in the Anthracite Region. Most of the available data regard-

ing surplus water in the bituminous fields are given in gallons of water per acre of mined out coal instead of so many gallons or tons of water to be disposed of per ton of anthracite produced as in the anthracite mines.

Following extensive investigations on the water flow from bituminous coal mines, Eavenson^{64,65} according to reports on the famous Indian Creek court case, estimated 2,000 gallons of water per acre of exhausted coal per day as an average for a 500-acre mine. The drainage from this and some other mines had caused serious pollution in a large water supply reservoir in western Pennsylvania, which was used by some municipalities and the Pennsylvania Railroad as a source of their respective water supplies.

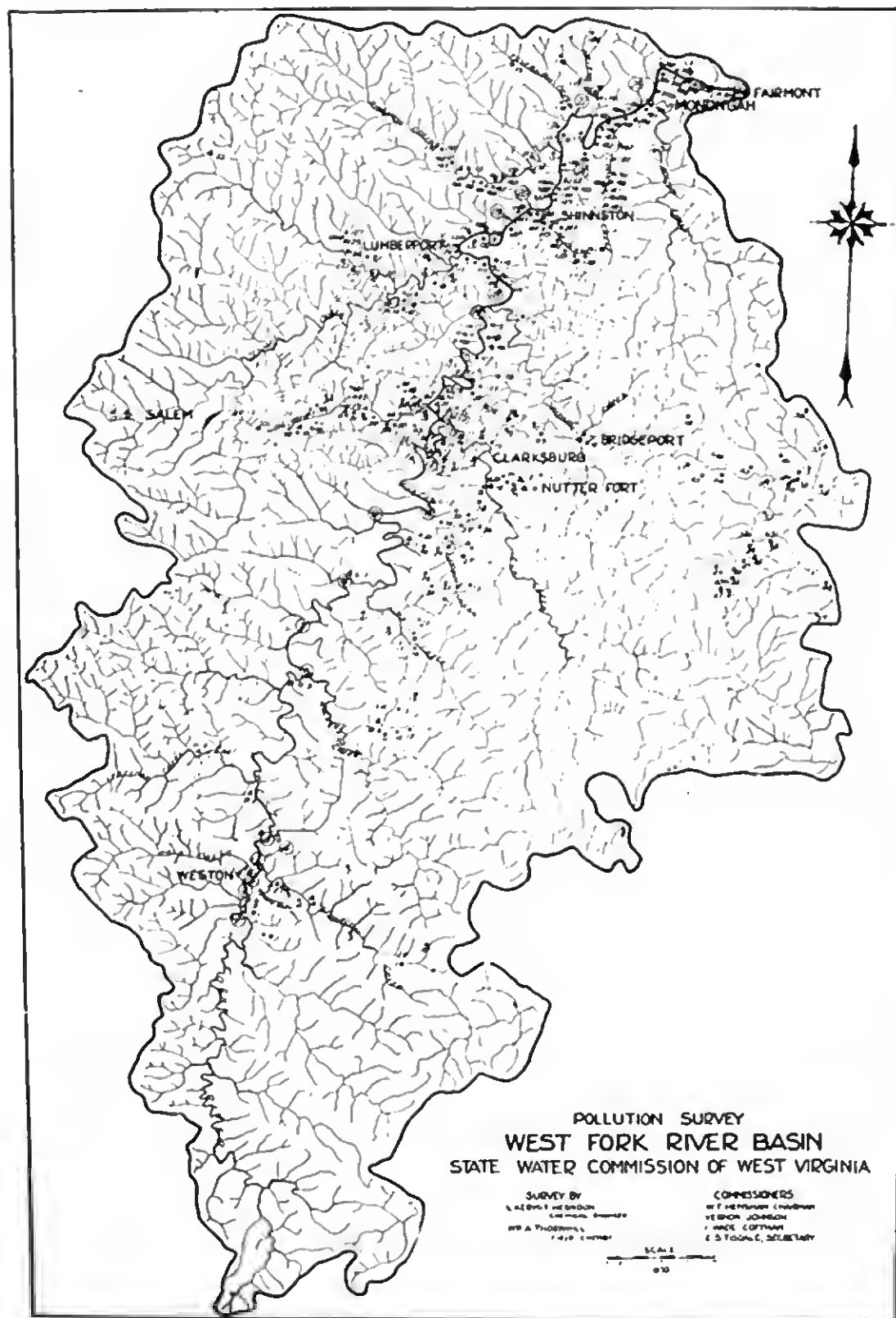
Following investigations made at some 250 bituminous coal mines in central and western Pennsylvania, Crichton^{52,53} concluded that a fair average was 1,100 gallons per mined out acre per day. One exceptional mine produced 10,000 gallons per acre per day, but there were many mines which produced less than 1,000 gallons of water per acre per day.

Herndon,^{94,95} and Herndon and Hodge,⁹⁶ following surveys of coal mines and effluents therefrom on several watersheds in West Virginia, stated that for coal mines in that State, 1,000 to 1,100 gallons of water per acre exhausted coal per day was an approximate average. They found that some of the smaller coal mines produced only around 500 gallons per acre per day, and some of the larger mines had flows of from 2,000 to 3,000 gallons per acre per day. This was different from the investigations of Crichton,⁵² who stated that with the increasing size of the mine the volume of water flow per acre per day became less. However, results of the surveys indicated that there was no definite relation between the size of the mine and the volume of water produced per acre of exhausted coal per day.

An illustration of the drainage survey made by Herndon⁹⁴ of the watershed of the West Fork River Basin, West Virginia, is shown in Figure 6. From surveys such as these made on other streams in West Virginia, it was estimated that an average of 168,349,000 gallons of mine drainage containing the equivalent of 2,876,000 pounds of concentrated sulfuric acid were daily flowing into the river systems from the coal mines of the State.¹⁰²

In other states in the Ohio River Basin a number of pollution surveys were carried out and it was apparent the bituminous coal mines were contributing millions of gallons of water, much of it rather acid in reaction, to the Ohio River.

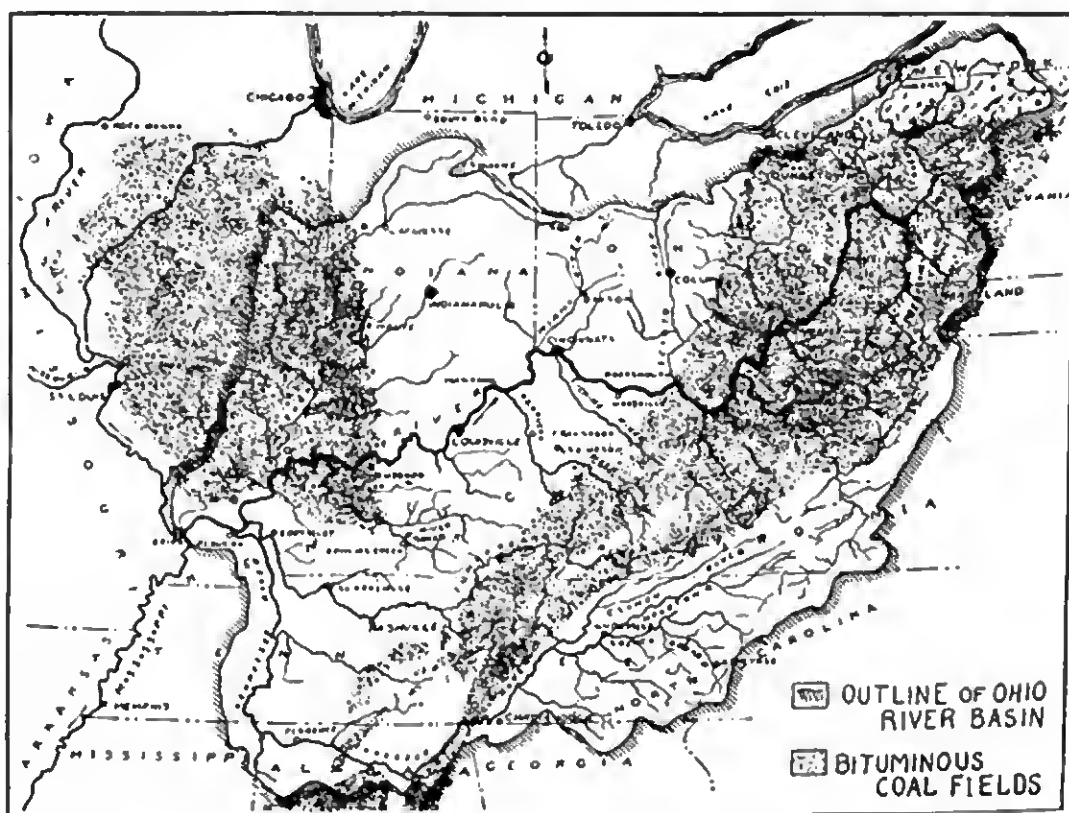
The Ohio River Basin comprises an area of nearly 204,000 square miles, Figure 7, and is inhabited by about 19,000,000 people. The river is a source of water supply for many municipalities and manufacturing



(Courtesy, West Virginia University Eng. Expt. Sta. Tech. Bull. No. 4, May, 1931)

FIGURE 6. Drainage survey, West Fork River Basin, West Virginia
 Legend: ● and ▲ indicate coal mines investigated

industries, and the volume of water contributed from coal mines is an important source of supply in some sections of the area. Not all bituminous coal mines produce acid water. In the survey of West Virginia water supplies, Hodge¹⁰² found 21 towns which utilized mine drainage for their local water supply. There are also some municipalities in Pennsylvania which utilize mine water. However, these are the exceptions and not the general rule in the Ohio River Basin.



(Courtesy, *Ind. Eng. Chem.*, 29, 1050, 1937)

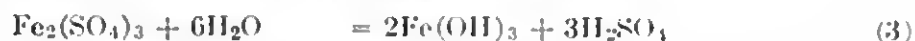
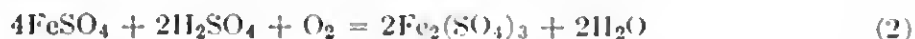
FIGURE 7. Ohio River Basin showing the Ohio River and its principal tributaries and approximate locations of bituminous coal fields. (Compiled from maps of the United States and State Geological Surveys)

Acid Mine Drainage

Investigations and Theories on the Formation of Acid Mine Drainage. This problem has been extensively investigated from both the chemical and, in recent years, the bacteriological standpoints. It is apparent that the formation of the acid mine drainage involves the oxidation of the sulfidic materials in coal. It has also been shown that the formation of the iron sulfates, aluminum sulfates, and other compounds in the coal mines results soon after the oxygen and moisture of the air come in contact with the coal, especially if the coal is finely divided. This has

suggested a study of the forms in which sulfur occurs in coal, and this factor is discussed later.

The chemical equations often published to illustrate the probable method of formation of the acid mine drainage are as follows:



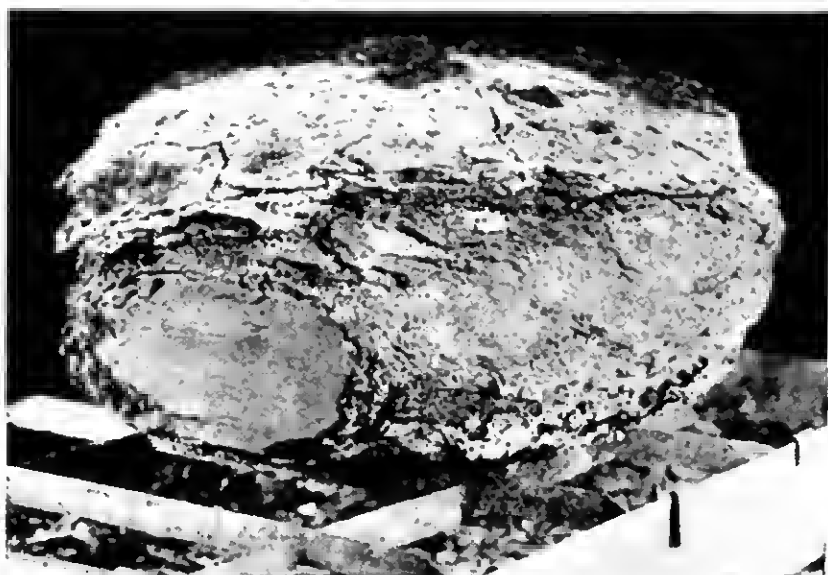
The mechanism of these reactions was studied by Burke and Downs.³¹ They suggested that the formation of the iron sulfate and sulfuric acid is the result of two consecutive reactions: the surface reaction between iron sulfide and dissolved oxygen from solution which proceeds slowly, and the oxidation of sulfur dioxide by additional oxygen and water to form the sulfuric acid according to the equations:



Many laboratory investigations have been made by Stokes,²⁰² Winchell,²³³ Nelson, Snow, and Keyes,¹⁵³ and Braley²⁷ on the oxidation of iron pyrites and marcasite and on different sulfur-containing materials occurring in the coal mines. The rates of oxidation of these materials appear to vary between wide limits, probably depending on the properties of the liquid or gaseous environment, the fineness of the sulfidic material, temperature and other physico-chemical factors. Some early reports were to the effect that the iron pyrite when subjected to aeration in water suspension oxidized very slowly, if at all, while marcasite under similar conditions oxidized quite rapidly, and crushed sulfur ball material oxidized very rapidly. The presence of traces of ferric sulfate in the water accelerated the rate of oxidation of the solid sulfidic material present in some experiments. According to Stokes, both pyrite and marcasite are decomposed by circulating alkaline waters which carry away the sulfur as alkaline sulfates or thiosulfates and the iron remains as hematite or hydrated ferric oxide. The results of atmospheric oxidation of a sulfur ball are shown in Figure 8. The scaled-off material was acidic. Results of analyses made by the author, of so-called "sulfur-balls," showed that some of them were composed largely of iron sulfides, others were mainly iron carbonate and silicate, possibly a form of impure ankerite or siderite.

In recent years attention has been directed toward the possible role which microorganisms may play in the formation of the acid mine drainage, and several investigations have been initiated along those lines, the results of which are briefly described in another section of this chapter.

Sulfur-Containing Materials in Coal. The production of acid mine drainage soon after the coal in the seam comes in contact with the moisture and oxygen of the atmosphere indicates that the acid mine drainage results from the oxidation of the moist sulfuritic substances in the coal. In their studies of the forms in which sulfur occurs in bituminous coals, Powell and Parr¹⁶⁷ found four forms, as follows: Sulphide S, principally as the iron sulfides, pyrite and marcasite, both have the formula FeS_2 ; sulfate S, mainly as calcium sulfate, which is usually present in trace amounts in freshly mined coal, but after being stored for



(Courtesy, Bituminous Coal Research, Inc.)

FIGURE 8. Sulfur ball showing disintegration after exposure to outside atmospheric conditions for six weeks

two or three years the major portions of the inorganic sulfur in the coal may be as sulfates, probably formed by slow oxidation of the sulfides originally present in the coal; organic S, in two forms, phenol soluble resinic S, and phenol insoluble humus S. In some of the coals examined, the organic sulfur constituted a larger proportion of the total sulfur than was usually anticipated. No free sulfur was found in any of the samples, but it may be present in very small quantities in some coals.

The distribution of the different forms of sulfur in the coal seams has been investigated by Yancey and Fraser.²³⁵ They found that the major inorganic compounds, iron pyrite or marcasite, were extremely irregular in their distribution in the coal beds. The iron sulfides were present in various sizes and shapes, which were classified as: microscopic pyrite, spherical particles varying from a few microns to 100 microns in diameter; fine disseminated visible pyrite; and coarse pyrite. Much of the

fine visible pyrite occurred in the forms of "cats faces," small flakes, thin bands less than 0.25 inch in thickness, veinlets or flakes of variable structure, called "spar sulfur" by the miners. The veinlets are difficult to separate from the coal by hand picking and they form slurries when the coal is crushed and sent to the coal washery, thus limiting the removal of sulfur from the coal. The coarse pyrite occurred in small, medium (2 to 4 inches), and large formations up to the so-called "nigger heads" or "sulfur balls," which range in size from 4 inches up to around 3 to 5 feet in dimensions. The concentration of pyritic sulfur in coarse bands or lenses is the main cause of the irregularities in the distribution of total

TABLE 5. PYRITIC AND ORGANIC SULFUR IN VARIOUS COALS†¹⁶⁷

(Values given in table in per cent, on a moisture-free basis)

Location of Mine	Coal Bed	Total Sulfur	Pyritic Sulfur	Organic Sulfur	Organic Sulfur as per cent of Total Sulfur
Clearfield Co.,* Pa.	C & D	3.48	2.77	0.71	20.4
White Co., Tenn.	Sewanee	4.87	3.59	1.17	24.0
Pike Co., Ky.	Freeburn	0.46	0.13	0.33	72.0
Williamson Co., Ill.	No. 6	1.83	1.04	0.79	43.2
Greene Co., Ind.	No. 4	1.66	0.89	0.77	46.4
Franklin Co., Ill.	No. 6	3.29	1.99	1.30	39.5
Webster Co., Ky.	No. 12	1.48	0.70	0.78	52.6
Union Co., Ky.	No. 9	3.46	1.65	1.81	52.5
McDowell Co.,** W. Va.	Pocahontas				
	No. 3	0.55	0.08	0.46	83.7
Letcher Co.,** Ky.	Elkhorn	0.68	0.13	0.51	75.0

†Courtesy, University of Illinois, *Eng. Exp. Sta. Bull. No. 125* (May, 1921).*H. F. Yancey and Thomas Fraser, *Coal Industry*, 3, 36 (1919).**A. R. Powell, *J. Ind. Eng. Chem.*, 12, 889 (1920).

sulfur in the coal seams, the fine disseminated pyrite being much more uniformly distributed. Microscopic pyrite was found in all samples examined, but its amount could not be accurately determined because of its wide variation even in the same section. The organic sulfur was found to be usually fairly uniformly distributed through the vertical span of the bed, but the quantities varied considerably in different areas of the seams. There appeared to be no definite relationship in the occurrences of organic and pyritic sulfur and the organic sulfur was not concentrated with or around the pyrite deposits. The proportion of organic sulfur to total sulfur in different coals varies between wide limits and in low sulfur coals makes up a greater percentage of the total sulfur than it does in high sulfur coals as shown in Table 5. In 49 of the 104 face samples taken in three coal beds in Illinois and Kentucky, the organic sulfur exceeded that of the pyrite, hence it often makes up

a greater percentage of the total sulfur of the coal than is generally recognized. The large pyrite formations may be removed by hand picking, and the intermediate sizes by coal washeries. The microscopic pyrite and often much of the fine disseminated pyrite and the organic sulfur substances are not removable by such methods and thus limit the proportion of total sulfur that can be removed from the coal by present coal cleaning or preparation installations. The accumulations of coal fines, often called "bug-dust" and "sulfur-mud," and other wastes containing sulfuritic substances left in the mines or in adjacent dumps or "gob-piles" are the sources of much of the acid or potentially acidic compounds found in acid mine drainage. Therefore, good housekeeping in the coal mines and proper disposal of all sulfuritic wastes are important factors in combating stream pollution by acid mine drainage.

Bacteria in Acid Mine Drainage. The probability that microorganisms play a part in the formation of acid mine drainage has been suspected for many years. Powell and Parr¹⁶⁷ observed that with duplicate sterilized samples of coal, the samples inoculated with old partially oxidized coal showed little difference after 19 days storage, but after 88 days storage the inoculated samples of coal showed decided increases in the quantities of soluble sulfur present compared to that found in similar samples which had been sterilized but not inoculated. Research on the microorganisms active in the oxidation of sulfur-containing materials in soils was carried on by Waksman and Joffe.²²⁸ They isolated and developed cultures of *Thiobacillus thiooxidans*, a new sulfur oxidizing microorganism, and described its characteristics. Studies by Carpenter and Herndon³⁷ were carried out on samples of coal from five different mines with sulfur contents varying from 2.8 to 3.7 per cent. The coals were pulverized to pass a 100-mesh screen. Duplicate 5-gram portions of each sample were placed in separate 500-ml flasks containing 200 ml of distilled water. Half of the flasks containing the coal samples were sterilized in an autoclave at a pressure of 15 lbs for a period of thirty minutes. The cotton stoppers placed in the flasks when they were sterilized were allowed to remain and the flasks were then stored in a dark cabinet. Every thirty days the flasks were shaken and the samples were analyzed at intervals from 30 to 690 days. The results showed rather conclusively that a larger percentage of the sulfur in the coal became soluble in the unsterilized as compared with the sterilized samples. Through further investigations along this line, Carpenter and Davidson³⁶ were able to isolate a microorganism from the samples which showed the highly soluble sulfur contents. They considered the microorganism was related or quite similar to *Thiobacillus thiooxidans*, but it was not definitely identified.

The results of investigations started by Hodge and Hinkle¹⁰⁴ also indicated that microorganisms played an important role in developing the acidity of some coal mine waters. These investigations were carried out on the Research Fellowship sponsored by Bituminous Coal Research, Inc., at the Engineering Experiment Station, West Virginia University. Some of the observations were summarized in a paper by Hodge, Kochler, and Hinkle.¹⁰⁸ They found that, with duplicate samples of water collected from certain coal mines, if one sample was stored in a cold room slightly above freezing temperature, and the other sample was stored in the laboratory at room temperature, the latter sample soon underwent hydrolysis with precipitation of yellowish-brown to reddish-brown insoluble matter on the bottoms and sides of the containing glass jugs, and the mine water became decidedly acid. On the other hand, the duplicate samples stored in the cold room did not undergo any noticeable changes during long periods of storage. Synthetic mine waters prepared in accordance with the analyses of natural mine waters and under sterile conditions did not undergo any noticeable changes on storage at cold room or laboratory temperatures for several weeks. However, when some of the samples of the synthetic mine waters were inoculated with water from a natural mine drainage which was undergoing hydrolysis, the inoculated sample of synthetic mine water soon started to hydrolyze and form deposits of insoluble material similar to those previously described, and the water became quite acid. The uninoculated samples of synthetic mine water did not undergo the changes observed in the inoculated samples. The work on this Research Fellowship was continued and the results have been reported in papers by Colmer and Hinkle,⁴³ and Hinkle and Kochler,⁹⁷ to the effect that two microorganisms have been isolated which accelerate the hydrolysis of mine waters with resulting increases in their acidities and the precipitation of hydrated iron sulfates. One of the organisms was considered to be *Thiobacillus thiooxidans*, which had been previously isolated from the acid mine drainage of some bituminous coal mines. The results of further investigations on this Fellowship have been reported by Colmer, Temple, and Hinkle,⁴⁴ Temple, Colmer, and Kochler,²⁰⁹ and by Temple and Colmer.^{207,208}

Another microorganism has been isolated from the acid mine water which oxidizes both thiosulfate and ferrous sulfate. A study of this bacterium was carried on in a highly acid inorganic medium consisting of ferrous sulfate, magnesium sulfate, ammonium sulfate, and distilled water. The culture on this type of medium has been carried on for over a year by making transfers approximately every two weeks. Large amounts of iron were oxidized when added as successive increments of ferrous sulfate. They conclude that the oxidation is bacterial and not purely chemical.

The oxidation may be stopped by adding any of the usual protoplasmic poisons. The rate of oxidation is not constant, but increases to a maximum on a curve resembling the ordinary growth curve. The time required for oxidation of the iron sulfate increment used decreased eventually from 10 days to less than 24 hours. The relation between the results of these many researches conducted on the Bituminous Coal Research, Inc. Fellowship are considered to be significant as offering partial explanation to the chemical reactions which take place in the formation of acid mine drainage.

The increasing importance of acid mine drainage as a pollutant of the waters of the Commonwealth of Pennsylvania led the Sanitary Water Board, Department of Health, Commonwealth of Pennsylvania, to establish, in 1946, a Multiple Fellowship at the Mellon Institute of Industrial Research to study problems in the formation of acid mine drainage and possible methods for abating stream pollution from this source. The work on the Fellowship has involved field investigations and laboratory research along both chemical and bacteriological lines. A brief résumé of progress in the latter field may be obtained by a study of papers presented by Leathen and Madison,¹²⁴ Leathen and Braley,^{125,126} and Leathen, McIntyre, and Braley.^{127,128} They have found *Thiobacillus thiooxidans* in a number of mine waters, also several autotrophic bacteria which also appear to play a role in the formation of the acid mine drainage. It was impossible to separate some of the other bacteria from the *Thiobacillus thiooxidans* by the use of any of the known bacteriological media. A medium has been developed, however, by which the desired separation has been obtained. The major chemicals used in the composition of this medium are as follows:

Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$	0.15 g
Potassium chloride, KCl	0.05 g
Magnesium sulfate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.50 g
Dipotassium phosphate, K_2HPO_4	0.05 g
Calcium nitrate, $\text{Ca}(\text{NO}_3)_2$	0.01 g
Distilled water	1,000. ml.

Sterilization is accomplished by autoclaving for 15 minutes at 15 psi. A stock solution of ferrous iron is prepared as follows:

Ferrous sulfate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	10 g
Distilled water	100 ml.

This solution is sterilized by filtration, using either Berkefeld or Fisher-Jenkins filters. If refrigerated, the solution will remain sterile and without appreciable oxidation for several weeks. This medium overcomes many of

the objections which have been found in trying to use other media for bacteriological research on acid mine drainage. It is to a certain extent a differential medium and can be altered within limits to facilitate biochemical and physiological studies of microorganisms. This medium has now been used for over two years by Leathen, McIntyre, and Braley in their studies on the rapid bacterial oxidation of ferrous iron to the ferric state in acid mine waters. During this same period stock cultures of the iron-oxidizing bacteria have been maintained in this medium without any noticeable changes. This medium is being used in further studies of the bacterial action in oxidizing the common sulfuritic constituents in bituminous coal and in the role of bacteria in the formation of acid mine drainage.

Acid Mine Drainage in the Anthracite Region. Many of the mines in the Anthracite Region of Pennsylvania discharge acid mine drainage. The extent of the acid mine water has been investigated by the staff of the United States Bureau of Mines. Felegy, Johnson and Westfield⁷² reported on the results of tests made on 327 samples of mine waters collected during 1941 and 1946, and the acid-mine-drainage problem is evidently Region-wide. The samples were collected from anthracite mines in the Northern, Eastern Middle, Western Middle, and Southern Anthracite Fields. Nearly all the samples were acidic with pH values as low as 2.4 and ranging up to 6.8. Only 5 of the samples had pH values of 7.0 or slightly higher. The pH values of the majority of the samples ranged from about 2.5 to 6.0. A few of them which had pH values slightly lower than 7.0 gave alkaline reactions when titrated with phenolphthalein or methyl-red indicator. They also tested 108 samples of water collected from the main rivers of the region—the Lackawanna, Susquehanna, Lehigh, and Schuylkill—and included one sample from the Delaware River. The majority of these samples were alkaline in reaction. A summary based on these investigations indicated a total of 1,821,297 tons of mine water discharged daily from all the mines in the Anthracite Region. The estimates of the daily free-acid load was 445.69 tons (as H_2SO_4) and of the daily total-acid load as 945 tons (as H_2SO_4). They give data indicating that the cost for neutralization of the acid mine drainage would vary at four different collieries from \$0.09 to \$0.795 per ton of coal produced. They conclude that the cost of neutralization of all the acid mine drainage in the Anthracite Region would be exorbitant. The sealing of abandoned anthracite mines was considered impractical because of the topography and the geological strata of the region. The mine drainage was considered to have some beneficial effects in neutralizing the alkaline wastes and municipal sewage discharged to the streams. In flowing from the anthracite fields the major rivers pass through extensive limestone areas which aid

in neutralizing the acid mine drainage so that the river waters in the highly populated southeastern areas of Pennsylvania are neutral or slightly alkaline.

The investigations were continued after 1946 and the results have been summarized by Ash, Felegy, Kennedy, and Miller.⁵ Many more samples of coal mine and river waters were collected, tested, and chemically analyzed. Analytical data for samples of mine water from two typical anthracite mines are given in Table 6. The general results

TABLE 6. ANALYTICAL REPORT OF SAMPLES OF MINE WATER IN TWO TYPICAL ANTHRACITE MINES⁵

Item	Mine A	Mine B
Discharge volume (gal min.)	2,500	900
pH	3.7	6.2
Free acid (ppm)	124	¹ 4
Total acid (ppm)	466	13
Silica (SiO ₂)	14	9.6
Aluminum (Al)	17	1.9
Iron (Fe)	22	.2
Manganese (Mn)	10	4.6
Calcium (Ca)	95	34
Magnesium (Mg)	55	12
Sulfate (SO ₄)	746	172
Chloride (Cl)	9	2.4
Dissolved residue dried at 103°C	1,070	268
Suspended matter dried at 103°C ²	131	7.3

¹Alkaline.

²ppm of unfiltered water.

obtained as to acidity or alkalinity of the mine waters and river waters were quite similar to those previously stated. The damaging and costly effects of floods in the anthracite regions and the uses of waters for washing coal and other industrial purposes are described. The estimate by Roos¹⁷⁴ that 1,100 gal of mine water are utilized in preparing each ton of anthracite mined is taken as a basis for computing the gallons of water used per minute in the preparation of coal in the anthracite field. The total volume of water so used is estimated as 66,536 gal per minute in the major collieries of the Pennsylvania Anthracite Region. The investigations also included the examination of samples of water pools in strip-mine excavations. Nearly all the samples were slightly acid, having pH values ranging from 3.7 to 7. The only samples showing any trace of alkalinity were two obtained in the Southern Field, and only five samples, also taken from stripping excavations in the Southern

Field, were markedly acid. Apparently the acidity or alkalinity of the river that drained the anthracite region is not greatly affected by the drainage from the stripping excavations, especially in view of the high acidity of the mine waters from the underground mining operations.

The treatment of acid wastes is described with special reference to the neutralization of acid mine waters by calcium and magnesium oxides and hydroxides, and by the corresponding limestones. At a few anthracite mines the acid mine drainage is neutralized by applying lime or limestone. Billharz²² has described a similar treatment successfully applied to acid mine waters from metal mines. The problem of the acid mine drainage in the anthracite region is closely associated with the disposal of the immense volumes of surplus water coming from the anthracite mines. The acid quality of much of the mine drainage is a factor which must receive serious consideration in planning the proposed large drainage tunnel for the anthracite region. However, investigators with the Bureau of Mines believe that the tunnel may be so designed and constructed as to solve both the surplus water and acid mine drainage problems.

Drainage from Some Strip Mines. The rapid development of the strip mining of coal in both the bituminous and anthracite regions has resulted in further problems in connection with the pollution of streams by acid mine drainage. There is no doubt that some of the strip pits develop acid waters which may flow out naturally or be washed out following heavy rains, thus adding peak loads of acid drainage to the receiving waterway. The author has made investigations of the waters in and from strip mining operations in West Virginia, Pennsylvania, and eastern Ohio. A great many of the strip pits were practically dry while others contained pools of water and some had water flowing from them. Surveys were made of many strip mines and the watercourses in the respective mining areas. The results obtained over an extended area, which was known as a limestone country, showed that only two of the many strip mining operations examined contained acid water, and all of the major streams in that territory were slightly alkaline in reaction. In another section of the state with shale and sandstone as the major strata, cut by the strip mining operations, several strip pits were found to contain acid water, but none of the major streams in that area were acid. Apparently the nature of the drainage from strip mines depends to a considerable extent on the geological strata of the region, the amount and quality of the coal and refuse left in the pits, the quantity of water in the mined-out sections, and the time of contact between the water and the residual coal. Under the newer laws in some of the states, the mining companies are required to back-fill the excavations as soon as mining is completed, and to contour the back fill as nearly as possible

to the original topography of the mined-out area. This procedure has greatly reduced the quantity of acid mine drainage from strip mining operations in the bituminous fields.

Another method recently developed in Pennsylvania is to have the back-fill operations follow closely on the mining operations. By this method the usually small amount of coal and refuse left on the mine floor and in the high wall is covered with earth before the sulfuritic substances are oxidized to soluble compounds. This reduces the time factor, often important in the formation of acid mine drainage, and makes the over-all back-filling operation more readily attained. In Indiana, Illinois, Ohio, Pennsylvania and West Virginia, and probably in other states, a good many of the strip mined waste lands have been back-filled and planted with trees or made into pasture lands, and quite a few have been developed into parks and recreational areas. This eliminates the unsightly appearance of many strip-mine areas and renders some of the land agriculturally productive and other sections useful for recreational purposes. This indicates the modern trend in handling the strip-mining problem. The subject of mine drainage from strip mines in the anthracite region is discussed under the section on Acid Mine Drainage in the Anthracite Region.

Detrimental Effects of Acid Mine Drainage. The corrosive effects of the acid mine drainage in the streams causes considerable damage to ships and barges, locks and dams, and the culverts and bridges. Also, such water is aggressive and attacks pipelines and plumbing fixtures unless neutralized at the municipal water plant. Estimates of damage along these lines have been made by Roberts,¹⁷³ by the United States Army Engineers,⁶⁻²² and by the United States Public Health Service.¹⁶⁰ Many of the rivers in the Ohio River Basin are canalized and, according to Crohurst,⁵⁴ impounding of acidic waters by these dams, especially during periods of low stream flow, results in more rapid deterioration of the river structures and locks than would be occasioned by natural water. The detrimental effects of excessive amounts of acid mine drainage in the streams also extend to aquatic life. The acidic waters may destroy the fish, and the precipitation of the basic iron sulfates and oxides (from the "red water" and "yellow boy") interfere with the propagation of fish life, and with nature's self-purification of streams, according to Purdy,¹⁷⁰ and Stevenson.^{199,200} To make such waters suitable for municipal supplies it often requires expensive chemical, settling, and filtration treatments. Otherwise, the water may be unfit for drinking or household purposes and may cause unsightly reddish-brown spots on fabrics in the laundry, and scum on wash bowls, sinks and tubs. For many industrial uses the waters would also have to be given extensive

treatments or the rates of corrosion and scale formation in pipelines, boilers, and other equipment would probably be excessive.

Other investigations along these lines have been reported by Hodge and Newton,¹⁰⁶ Hodge and Niehaus,¹⁰⁵ Hodge,¹⁰⁰ Young,²³⁷ and Morgan.¹⁴⁷ In 1936, Davis⁵⁶ estimated that the rivers flowing through the Pittsburgh District carried a load of acid equivalent to that of 9,000 tons of sulfuric acid per day. The total load of sulfuric acid equivalent for the entire Ohio River Basin was estimated during the Ohio River Pollution Survey at 2,500,000 tons per year.¹⁶⁰

The cost for treatment of stream waters caused by pollution from acid mine drainage has been continually increasing with the growth of the coal mining industry. Trax^{221,222} estimated the additional costs for such treatment of the Monongahela River water along the 50 miles of its course from the West Virginia line to McKeesport, Pennsylvania, at \$801,000 per year to the industrial and water works plants obtaining their supplies from that river. Estimates made by Young²³⁷ indicated that two large railroads operating in the Pittsburgh District expended over \$800,000 in the course of a year for locomotive boiler repairs required as a result of acid mine drainage in the river water. He also concluded that the extra cost for plumbing and water supplies to the population of Pittsburgh was \$3,000,000 per year. According to Drake⁶³ an all-time high of 3,000,000 lb of soda ash were used during 1931 to neutralize the Allegheny River water supplied to the city of Pittsburgh. The increased annual expenditures for treating the water used on two railroad lines in West Virginia have been estimated by Bardwell¹⁹ to be approximately \$75,000. The damages by acid water to navigation structures and floating equipment in the Pittsburgh area were estimated by the United States War Department²²⁷ as between \$500,000 and \$600,000 per year. Excessive corrosion of culverts in the highways of West Virginia caused by acid waters was estimated by Downs⁶² to be \$500,000 per year. The additional costs and losses to water purification plants and industries in West Virginia were placed by Tisdale and Lyon²¹⁷ at \$1,000,000. These are but a few examples of additional costs for water treatment occasioned by the acid mine drainage discharged into the streams in the Ohio River Basin. The Works Progress Administration¹⁶⁰ made conservative estimates of the extra costs due to damages caused by acid mine drainage in the states in the Ohio River Basin as about \$10,000,000 per year.

Methods Proposed for Reducing Pollution of Streams by Acid Mine Drainage. There have been many field investigations and considerable laboratory research directed toward developing procedures for reducing the volumes and objectionable properties of acid or potentially acid mine waters. The methods proposed may be classified as follows:

- (1) completely closing the mine;
- (2) impounding the mine drainage;
- (3) flooding abandoned mines;
- (4) dilution of the mine drainage;
- (5) chemical processes for the recovery of valuable products;
- (6) neutralizing the acid mine drainage with limestone or marl, lime, or soda ash;
- (7) diverting acid drainage to streams already hopelessly polluted;
- (8) diversion of surface waters from entry into the mines;
- (9) pumping the waters out of the mine as rapidly as possible; and
- (10) air-sealing abandoned coal mines and worked-out entries in active mines.

Coal mines have been completely closed in some cases but the practice involves certain hazards and has not become a general method of combating acid mine drainage.

Impounding the mine drainage has been satisfactory in a few mines, but in other mines the dams have failed and the out-rushing water caused serious damage to the receiving waterway and to downstream properties.

Some shaft mines have been flooded and in time the formation of acid mine water practically ceased. Leitch¹³⁰ reports the results of analyses of the waters in three closely adjacent coal mines. The reaction of the water in the completely flooded mine was practically neutral; that from the partially flooded mine was mildly acid and the water in the non-flooded mine was decidedly acid.

The suggestion that mine drainage be diluted with natural water sounds reasonable but the volume of dilution water would have to be exceedingly large to appreciably reduce the pH value of any quantity of acid mine drainage. Crichton^{52,53} states that it requires 80 to 100 gallons of fresh water streams having a natural alkalinity to neutralize one gallon of average acid mine water. Carpenter and Davidson³⁶ conducted experiments in which they found that dilution with distilled water would have to be around 4,000 times the volume of a mine drainage having a pH of about 2, in order to raise the pH to 5.2. Furthermore, the dilution method may not remove the acid-forming substances from the mine drainage and might be costly. Dilution could serve as an ameliorative measure, especially during periods of low stream flow, and beneficial results have been reported by the regulated flow of water impounded by some of the large Federal Government dams.

A method for recovering paint pigments from acid mine drainage was developed by Kaplan¹¹⁶ and patented by Kaplan and Reger¹¹⁷ of the West Virginia Geological Survey. The process worked out satisfactorily

on a laboratory scale and several pigments of varying colors were prepared, but the cost for recovery of the by-products on a commercial scale was too high and the process has never been industrially developed.

A natural supposition is that the acid mine drainage might be neutralized with a low-cost alkaline material. However, calculations based on the quantitative analysis of a fairly acid mine drainage and the volume of such drainage indicate that the cost for the chemicals would be excessive and in addition, there would be large quantities of sludge to be disposed of. Crichton⁵³ has estimated that construction costs to neutralize the acid from coal mines in central and western Pennsylvania would amount to approximately \$75,000,000. The annual cost for lime alone, on the basis of 15 cents per thousand gallons, would be between \$41,062,500 and \$68,000,000. The costs for handling and disposing of the estimated 1,852,000 tons of sludge resulting from the neutralizing reaction would have to be added to the above costs. He quotes Charles Dorrance, that to neutralize the mine drainage reaching the streams in the anthracite region (approximately 700,000,000 gallons per day) the cost would be nearly as large as for neutralizing the acid mine drainage from the bituminous coal mines in central and western Pennsylvania. Furthermore, after neutralizing with lime, the water would be very hard and the costs for softening the water have been estimated at some 70 cents to one dollar per ton of coal produced. These estimates were made in 1925-1926, and the volumes of mine water and costs for equipment, chemicals and labor have increased considerably during the past 25 years.

An industrial size plant for the neutralization of acid mine drainage was constructed about 1916, by the Frick Coal Company at its Calumet mine located in Westmoreland County, Pennsylvania. The construction and operation of this mine drainage neutralization plant have been described by Tracy²¹⁹ and by Campbell.³³ The mine water was obtained through 3 bore holes, 215 ft deep, and pumps delivered around one million gallons of mine water per 24-hour day. The plant was constructed for three main purposes: (1) to obtain water suitable for use in the operation of coke ovens and, with additional treatment, as boiler water; (2) to obtain a useful by-product. It was estimated that on neutralizing the mine drainage with lime, approximately six tons of marketable ferric oxide (Fe_2O_3) would be obtained; and (3) to abate stream pollution. During World War I a market was obtained for the oxide as a material to remove hydrogen sulfide from coal gas. However, after the end of the war, this market reverted to its former sources of a cheaper form of iron oxide for the gas purification purpose. Difficulties were also encountered in the disposal of the sludge formed, which was

stated to be too thick to pump and too slimy to shovel. The plant was operated for about six years and then was abandoned.

Analyses of the mine water and of the recovered product are given in Table 7.

TABLE 7

Part A. Analyses of Acid Mine Water Before and After Neutralization with Lime²¹⁹

Constituent	Analysis of Mine Water		Analysis of Treated Mine Water	
	Gr./U.S. Gal	Lb/1,000 Gal	Gr./U.S. Gal	Lb/1,000 Gal
Non-incerusting solids				
Na ₂ CO ₃	None	None	None	None
Na ₂ SO ₄	8.5	1.2	11.6	1.7
NaCl	0.9	0.1	0.9	0.1
NaNO ₃	None	None	None	None
Incerusting solids				
SiO ₂	3.8	0.5	15.5	2.2
Fe ₂ O ₃ + Al ₂ O ₃	26.6	3.8	56.6	8.1
FeSO ₄	5.5	0.8	8.5	1.2
Fe ₂ (SO ₄) ₃	59.3	8.2	None	None
CaSO ₄	46.6	6.7	131.2	18.8
MgSO ₄	8.3	1.2	17.4	2.5
H ₂ SO ₄	21.3	3.0	0.5	0.1
SO ₃ as H ₂ SO ₄	165.7	22.3	172.6	24.7
Suspended matter	14.8	2.1	100.3	14.3

Part B. Analyses of Suspended Solids and Recovered Product

Suspended Matter		Analysis of Product	
	(%)		Moisture-free (%)
SiO ₂	7.6	SiO ₂	13.0
		TiO ₂	0.3
Al ₂ O ₃	4.6	Al ₂ O ₃	10.3
		P ₂ O ₅	1.0
Fe ₂ O ₃	41.3	Fe ₂ O ₃	37.1
CaO	7.0	CaO	13.2
MgO	Trace	MgO	0.6
		K ₂ O	1.0
		Na ₂ O	0.7
SO ₃	19.1	SO ₃	11.6
		H ₂ O	4.8
H ₂ O	12.4	Combined above 105°C	6.4
		CO ₂	

Some of the difficulties involved in the operation of this plant have been related by Lyon.¹³⁹ It required approximately two years to develop the equipment to operate smoothly. Certain changes were made in the pumps, thickeners for the sludge, and in the dryers. Lyon reported

that around 10 tons of hydrated iron oxide, with a moisture content of about 20 per cent, were frequently obtained in a day's operation. However, the operating costs, compared to the values derived from the sale of iron oxide, as well as the over-all advantage of the partially purified water, were disappointing and the plant was closed.

A process for treating acid waste waters, and especially directed toward the treatment of acid mine drainage, was developed by Travers.²²⁰ This process consisted of constructing a box with a drain bottom, and filling the box with crushed porous limestone of a special type known as marl, somewhat similar to travertine. The acid mine water was caused to flow over and through the crushed marl, the treated effluent was clarified by settling and overflowed to the receiving waterway. This process was installed at a mine discharging into Elk Creek in Harrison County, West Virginia. It was operated for about two years and a marked improvement of the receiving waterway was reported. However, the process was too expensive and the plant was abandoned.

Probably the most recent experimentation on the neutralizing of acid mine drainage with alkaline chemicals was carried out under the Industrial Fellowship at Mellon Institute, sponsored by the Pennsylvania Sanitary Water Board. Here, laboratory research was conducted, a pilot plant was constructed and investigations were carried out neutralizing acid mine water with limestone, lime, and soda ash. The investigation was carried out by Braley, Beal, and Levy.²⁸ A bulletin describing the operation of the pilot plant and the results obtained was issued by the Pennsylvania Sanitary Water Board. Further discussions of the problem of treating acid mine drainage have been given by Braley²⁶ in which he reviews the progress made on the Fellowship during the past three years. The general conclusion formed as a result of the laboratory, pilot plant, and industrial waste installations for the chemical neutralization of acid mine drainage was that it involved too large a cost for practical consideration.

By diverting acid mine drainage to streams which are already hopelessly polluted, unpolluted streams can be maintained in a satisfactory condition. This method has been applied to some extent in Pennsylvania and under the revised laws passed in 1945 and 1947 the State may contribute funds to be used for diversion of acid mine drainage to badly polluted streams.

Diversion of surface waters from entrance into mines has, under certain conditions, considerably reduced the total acid flowing from the mines. Under other conditions, however, it has not been too successful.

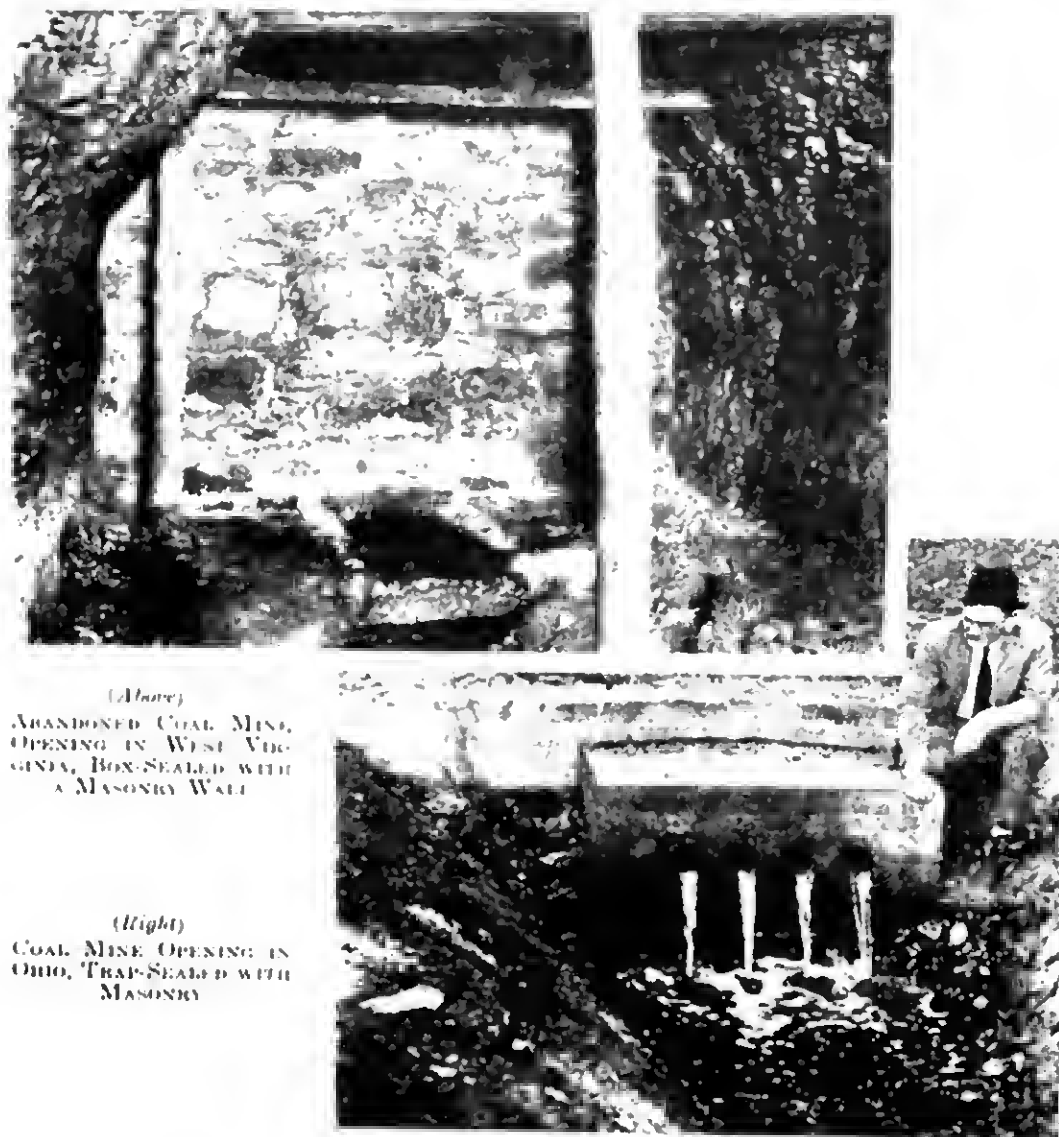
Pumping the water out of the mines as rapidly as possible will decrease the time factor, which is important in the formation of acid mine

drainage. Investigations on this factor of the problem are being carried out in cooperation with the Pennsylvania Sanitary Water Board Fellowship at Mellon Institute, and preliminary results indicate that this method may have decided value in reducing the quantities of acid mine drainage flowing from many mines.²⁷

The air-sealing of abandoned coal mines was carried out on an extensive scale from 1933 to 1941. The project was under the general supervision of the United States Public Health Service and was carried out in cooperation with the State Health Departments and the Corps of Engineers, U.S. Army. Many of the coal mining companies also contributed to some of the projects, which were carried out in nine of the coal-producing states which have streams tributary to the Ohio River. Comparatively little mine sealing was done in Maryland, Illinois or Virginia. Funds for the work were supplied by the United States Congress under grants to the Civil Works Administration, the Federal Emergency Relief Administration, and the Works Progress Administration.²²⁶

The project was undertaken partly because of the data obtained by extensive investigations carried on by Leitch¹²⁹⁻¹³² and Yant¹³³ and Sayers¹³⁴ and associates of the United States Bureau of Mines, and from the results of coal mine drainage and stream surveys made in West Virginia and Pennsylvania. The investigations by the Bureau of Mines staff showed that many of the abandoned mines, although inactive for 25 to 30 years, still produced acid mine drainage. In many instances, the mining property had reverted to the respective State because of unpaid taxes. Hence reduction of the acid mine drainage would have to be looked upon as a public health service for stream improvement. In their field investigations, Leitch and co-workers found certain mines which had been air-sealed by natural roof falls or by cave ins near the entrances to the mines. Analyses of samples of water collected from some of these closed or semi-closed mines showed that they were much less acid than other abandoned mines in the same vicinity which had not been accidentally air-sealed. Some laboratory experiments carried on by the Bureau of Mines confirmed the conclusions from the field investigations that air-sealing of the abandoned coal mines might reduce the quantity of acid drainage discharged into the streams. Some of the projects were undertaken to serve to some extent as relief measures for unemployment in the areas. The projects were carried on for about eight years and involved not only the air-sealing of mines but also diversion of surface waters from entrance into the mines. The more common types of mine seals and drainage openings have been described by Hatch.^{91,92} He classifies them into various types, as follows: masonry wall with a sewer trap somewhat similar to the S-trap in the plumbing

under the kitchen sink; masonry curtain wall with drain and overflow trough; masonry wall with earth fill and a possible sub-trap with overflow opening, Figure 9. Since the air must be excluded several types of dry seals were developed. These might be constructed of masonry walls, heavy earth fills, masonry walls with earth fills, and other types of



(Courtesy, Mine Sealing Programs, U.S. Public Health Service, 1937)

FIGURE 9. Two types of seals used in air-sealing abandoned coal mines

seals which were required by special conditions of the mine, regional topography, and construction materials readily available. Additional descriptions and diagrams of mine sealing have been given by Hoffert.¹⁰⁹

The total funds expended by the government on the mine-sealing projects were approximately \$5,500,000 and it was estimated that a

similar amount would be required to complete the mine sealing programs in the nine states involved. In the final report on this extensive mine-sealing program as presented to the Congress (Ohio River Pollution Survey, Final Report, ref. 160), the original mine acid load of free and potential sulfuric acid was estimated at 2,500,000 tons per year and the reductions in the load, as estimated from flow measurements and chemical analyses made before and after the sealing of the mines, amounted to 700,000 tons per year. Further estimates indicated that approximately 600,000 tons of the acid load per year could be prevented by sealing most of the remaining abandoned mines in the Ohio River Basin. Some further reductions might be made by modifications of the 1940 restrictions and then the ultimate residual acid load on the Ohio River and its tributaries would be about 600,000 tons per year. If fairly uniformly distributed, a large part of this residual acid load might be neutralized by alkaline wastes and the natural alkalinity of the streams. Of the total acid load, approximately 85 to 90 per cent was attributed to coal mines, active and abandoned, about 3.5 per cent to waste pickle liquor from the iron and steel mills, with the balance from other industries such as petroleum refining, by-product coking, and chemical manufacture, in which considerable quantities of acid are used.

It was already shown that because of roof falls, surface breaks or cave ins in the mines, geological faults, underground water tables and other conditions in the mining areas, total reductions in acid load could not be attained by air-sealing the mines, and continued maintenance of sealed conditions would be necessary to maintain the reductions obtained by the original sealing operations and diverting of surface waters. With the advent of World War II the mine-sealing program was abandoned in all the states, and neither the Federal Government nor the State legislatures provided funds for the maintenance of the mine seals which had been constructed. During this period the maximum production of coal was important and many of the mine seals were broken in order to obtain more coal from those mines. As a net result, at the end of World War II, many streams in the Ohio River Basin were nearly as acid as before the mine-sealing program was carried out. The only resumption of mine-sealing operations has been in Pennsylvania under funds appropriated by the legislature for that purpose. The program has been in operation about three years and since it takes considerable time for the mines to attain equilibrium after sealing, the eventual quantity of reduction of acid load has not been fully attained.

As a result of the many laboratory researches and field investigations which were made on the acid mine drainage problem, the following general conclusions were reached:

(1) The initial reaction in the formation of the substances which produce acid mine drainage is not as yet clearly understood.

(2) A great deal of pertinent information has been obtained regarding the several physico-chemical factors involved in the formation of the mineral sulfates in the coal mine waters and the role certain strains of bacteria have in accelerating the hydrolysis of the soluble iron sulfates to produce acid mine drainage.

(3) Good housekeeping in the coal mines, that is, the removing from the mines, as soon as possible, all the fines, sulfur balls, and other waste sulfidic materials would markedly reduce the production of acid mine drainage.

(4) Diversion of surface water from the mines and rapidly pumping or draining away all surplus water from within the mines would greatly reduce its time-of-contact with the sulfidic materials and thus tend to reduce the eventual formation of acid mine drainage.

(5) The air-sealing of abandoned coal mines and of worked-out sections of active mines may be another method for reducing the amount of acid mine water provided the seals are properly maintained.

(6) It is evident that developing methods for preventing the formation of the objectionable drainage offers more practical possibilities than does neutralization of the acid after it has been formed.

(7) The treatment and disposal of acid mine drainage is still one of the more important problems for stream improvement in the Ohio River Basin and in the Anthracite Region of the United States, and research should be continued until a satisfactory solution to the problem is developed.

DISPOSAL OF WASTES FROM THE COAL CARBONIZATION INDUSTRY

In studying the problems in the treatment and disposal of wastes from the coal carbonization industry, the fact becomes apparent that, in general, this industry has carried on a great deal of research and development work to recover usable substances from the originally waste products, and to develop uses for such by-products. This general trend has been different from that in some other industries, which have constructed large waste treatment plants instead of concentrating on trying to obtain usable materials or by-products from the wastes resulting during the necessary production processes. In this section brief descriptions will be given of the processes developed to recover and utilize the materials which were originally wastes, such as coal tar, light oil, ammonia, naphthalene, anthracene, and nitrogenous aromatic bases. A more extended discussion will be accorded the current wastes treatment and disposal plants for acid sludges, ammonia still wastes, and phenols.

The wastes treatments and disposal problems at city gasworks and by-product coke plants are very similar and they are not treated separately in this chapter.

The destructive distillation of bituminous coal is practiced largely for two main purposes: the production of coal gas and of metallurgical coke. Some coal is carbonized to produce coke as a smokeless fuel for general heating purposes. The methods of coking coal have progressed from the early earth pits through beehive ovens, inclined, vertical, and horizontal retorts, to the modern by-product coke ovens. According to Wilson and Wells⁶⁻²⁵ the first beehive ovens were probably used in England about 1763. A successful process for manufacturing illuminating gas by heating coal in inclined iron retorts was developed by William Murdock in 1792, and, in 1802, his house and the plant of his employer in Birmingham, England, were lighted with coal gas. The present Gas Light and Coke Company of London, England, was organized in 1812. The first three gas companies incorporated in the United States were in Baltimore, Maryland, in 1819; in Boston, Massachusetts, in 1822; and in New York City, in 1825; but the first gasworks built was in Baltimore, in 1816. While originally developed for lighting, the value of coal gas for domestic heating purposes was soon recognized, and with the growth of electric lighting, the primary interest of the coal carbonization industry in many places shifted to the manufacture of good fuel gas, metallurgical coke, and the recovery of usable by-products. For this three-purpose industry, the by-product coke ovens offered many advantages.

The value of the heat, tar, and volatilized gases wasted as a result of coal carbonization in beehive ovens was early recognized and many processes were proposed for recovering some of these values, but without any marked commercial success. Coke was the only useful product generally recovered and this amounted to about 55 to 65 per cent of the weight of the coal charged into the ovens. The coke was very suitable for use in the blast furnaces of the iron and steel plants. The development of processes and equipment for the recovery of useful substances from the materials volatilized when the coal was carbonized in retorts and by-product coke ovens became very active around 1860 in France, Germany, Great Britain and Belgium, and somewhat later in the United States; and chemical and engineering research along these lines is still in progress. In 1893, the Solvay Process Company built, in Syracuse, New York, the first by-product coke ovens erected in the United States. It was a battery of 12 ovens (there were 44,189 beehive ovens in the United States in 1893) and a primary reason for its construction was to recover ammonia from the volatilized products, since the ammonia was needed in the Solvay process for manufacturing sodium carbonate (soda ash), and some related chemical products. At first there were some

objections from blast furnace operators to the use of by-product coke, but it was soon demonstrated that cokes very satisfactory for use in blast furnaces and in iron foundry cupolas could be produced in by-product ovens. This factor, together with the value of the by-products recoverable from the carbonization of coal in by-product coke ovens, led to the construction of many such coking plants in the important industrial countries of the world. The first large batteries of by-product coke ovens built in this country for metallurgical purposes were those of the Illinois Steel Company constructed in 1906, in Joliet, Illinois. They were designed by Heinrich Koppers, a German scientist and engineer, who was formerly associated with the Otto Hoffman Company in Germany.

The very large demands in the United States during World War I for coke, ammonia, benzene, toluene and other products obtainable from the carbonization of coal in by-product ovens gave an impetus to the construction and operation of this type of plant. This resulted in such an increase in the production of by-product coke that its annual tonnage passed that of beehive coke in 1919. As shown in Table 8, the production of by-product coke has increased while that of beehive coke has decreased, until in 1930, the respective production data were: 45,195,705 tons, and 2,776,316 tons. During World War II the greatly increased demand for iron and steel led to reactivation of many of the batteries of beehive ovens, with a resulting increase in the production of beehive coke in 1945 to 5,213,893 tons, and an increased production to 62,094,288 tons of by-product coke.

Magnitude of the By-Product Coal Coking Industry

The quantities of beehive and by-product coke produced in the United States during certain selected years are given in Table 8.

World production of coke per year reached a peak in 1943, and was estimated at about 174,000,000 net tons; in 1948 world production, so far as data were available, was approximately 160,000,000 tons, of which the United States produced 42 per cent, Germany 12 per cent, Great Britain, France, Czechoslovakia, Poland, Belgium, and Canada, combined 24 per cent. For the Soviet Union, no precise data were available, but it probably ranked second to the United States in the production of metallurgical coke. In several European countries large quantities of gas-house coke are also produced, especially in Great Britain, which in 1947 produced around 15,000,000 net tons of gas-house coke. There are some thirty countries in the world in which coke is produced. In 1942, Japan produced about 6,500,000 tons of coke; in 1948, around 2,000,000 tons, which was approximately the same quantity as was produced in the Netherlands.

In South America there is one by-product coke plant in Brazil, and

TABLE 8. COKE PRODUCTION IN CERTAIN YEARS IN THE UNITED STATES^{226a}
(In short tons)

Year	Beehive Coke	By-Product Coke	Total
1880	3,300,000	...	3,300,000
1890	11,500,000	...	11,500,000
1893 ^a	9,500,000	10,000	9,510,000
1895	13,314,193	18,521	13,333,714
1900	19,457,621	1,075,727	20,533,348
1910	34,570,076	7,138,734	41,708,810
1916	35,646,224 ^b	19,069,361	54,533,585
1919 ^c	19,042,936	25,137,621	44,180,557
1920	20,511,092	30,833,951	51,345,043
1925	11,354,784	39,912,159	51,266,943
1929	6,472,019	53,411,826	59,883,845 ^d
1930	2,776,316	45,195,705	47,972,021
1932	651,888	21,136,842	21,788,730 ^e
1937	3,164,721	49,210,748	52,375,469
1945	5,213,893	62,094,288	67,308,181
1948	6,577,571	68,284,357	74,861,928 ^f

Courtesy, U.S. Bur. Mines, Dept. of Interior, *Minerals Yearbook* (1948).

^aFirst year in which by-product oven coke statistics are recorded.

^bAll-time peak production of beehive coke per year.

^cFirst year in which production of by-product coke exceeded that of beehive coke.

^dMaximum Pre-World War II production of oven coke.

^eDepression year, low production of coke.

^fMaximum all-time production of oven coke in the United States. These data do not include the coke made in retorts in city gas plants which in 1948 amounted to 127,218 net tons. Around 80 to 85 per cent of the by-product and beehive coke is used by the iron and steel industries.

construction of the first iron and steel plant and coke works in Chile was completed by the Koppers Company, Inc., in 1950.

The principal by-products—coal tar, ammonia, gas, light oils, naphthalene, pyridine, sodium phenolate, and sulfur—recovered from the by-product oven carbonization of coal during 1948 in the United States, and their values, are shown in Table 9.

The relative quantities of coke, breeze, gas, tar, ammonia, light oils, naphthalene, phenols and other products obtained per ton of coal carbonized vary widely depending on the kind of coal charged into the ovens, the rate of temperature rise, final temperature attained, types of coke ovens and equipment used, and other factors of operation. A general average per ton of good coking bituminous coal subjected to high temperature (900 to 1,100°C) carbonization might be as shown on the "Coal Products Tree" (Figure 10).

In 1948, the value of the by-product oven coke and breeze produced was \$883,303,496; of the beehive coke, \$79,804,061; and of recovered coal-

TABLE 9. COAL-CHEMICAL MATERIALS OBTAINED FROM COKE-OVEN OPERATIONS
IN THE UNITED STATES IN 1948^{1, 22a}
(Exclusive of screenings or breeze)

Product		Production	Sales			On Hand Dec. 31
			Quantity	Value		
				Total	Average	
Tar	gallons	738,755,106	402,407,480	\$11,957,748	\$0.104	32,828,763
Tar derivatives:						
Creosote oil, distillate as such	do	24,451,530	23,574,143	4,263,606	.181	907,351
Creosote oil, in coal-tar solution	do	10,533,183	9,461,370	1,643,720	.174	675,496
Tar acid oil	do	11,553,270	14,772,782	4,298,486	.291	440,195
Phenol	pounds	8,123,440	8,114,711	967,571	.115	219,493
Pitch of tar:						
Soft ³	net tons	388,599	3,391	101,353	29.862	10,052
Hard ³	do	248,316	572
Other tar derivatives ⁴		2,276,559
Ammonia:						
Sulfate:						
From coke-oven ammonia	pounds	1,661,365,037	1,665,530,716	35,561,991	.021	47,850,209
From purchased synthetic ammonia	do	61,498,005	60,720,455	1,600,154	.026	877,550
Liquor (NH ₃ content)	do	49,505,251	46,649,246	1,617,277	.035	992,781
				\$37,179,268
Sulfate equivalent of all forms ⁴	do	1,859,386,011	1,852,127,700	51,821,345
NH ₃ equivalent of all forms ⁴	do	464,846,510	463,031,925	12,955,336
Gas:						
Used under boilers, etc.	M cubic feet	7994,852,626	33,152,841	4,086,099	.123	...
Used in steel or allied plants	do		369,457,173	57,728,546	.156	...
Distributed through city mains	do		169,347,914	58,229,890	.311	...
Sold for industrial use	do		35,852,904	5,511,461	.154	...
		7994,852,626	607,810,835	125,555,996	.207	...
Crude light oil	gallons	*256,089,065	17,642,761	2,058,469	.117	3,794,999
Light-oil derivatives:						
Benzol:						
Motor	do	9,014,336	8,552,175	1,171,754	.137	532,143
All other grades	do	149,998,882	149,124,481	28,758,324	.193	5,696,201
Toluol, crude and refined	do	28,448,259	28,181,798	6,825,957	.240	877,502
Xylol, crude and refined	do	7,285,338	7,265,770	1,815,895	.250	408,673
Solvent naphtha	do	5,742,697	5,459,112	958,373	.176	359,583
Other light-oil products ⁵	do	8,061,571	5,525,753	631,816	.114	346,979
		208,551,083	204,409,092	40,162,119	.196	8,221,081
Naphthalene, crude	pounds	105,816,670	102,827,490	4,515,867	.014	5,119,129
Pyridine:						
Crude bases (dry basis)	gallons	416,591	383,824	392,366	1.022	105,004
Refined or 2 ^o	pounds	1,071,089	1,099,574	747,897	.680	15,721
Sodium phenolate	gallons	2,043,589	2,079,536	324,819	.156	108,493
Sulfur	pounds	6,814,528	7,644,030	108,752	.014	1,617,866
Other coal-chemical materials ¹⁰		511,960
Value of all coal-chemical materials sold				267,126,556

Courtesy, U.S. Bur. Mines, Dept. of Interior, Minerals Yearbook (1948).

¹ Includes products of tar distillation conducted by coke-oven operators under same corporate name.

² Softening point less than 110°F. Includes some medium pitch of tar reported by 2 producers.

³ Softening point over 160°F.

⁴ Cresols, cresylic acid, crude anthracene, fuel oil, pitch coke, road tar, tar paint, and refined tar.

⁵ Excludes value of sulfate made from purchased synthetic ammonia.

⁶ Excludes sulfate made from purchased synthetic ammonia.

⁷ Includes gas used for heating ovens and gas wasted.

⁸ Refined on premises to make derived products shown: 242,956,216 gallons.

⁹ Benzol still residue, dicyclopentadiene, orthoxylene, and vented vapors.

¹⁰ Ammonium thiocyanate, cyanogen sludge, picolines, secondary oil, and sodium prussiate.

chemical materials, \$267,126,556. The total value of these products was \$1,230,234,113. In addition there were the values of the gas, coke, and recovered by-products from the city gasworks, which are not included in the above given data. Hence, the coal carbonization industry in the United States is one of the few billion dollar per year industries. If all

the coal carbonized had been coked in beehive ovens the \$267,126,556 worth of by-products would have been lost and about 5 to 7 per cent less coke obtained from the coal processed. The change from beehive to by-product oven carbonization of coal resulted in a large reduction of atmospheric pollution, but did cause some water pollution, which has been greatly reduced through the development of processes for the recovery of the coal-chemical materials shown in Table 9. However, there is still some water pollution caused by certain effluents from by-product coke and tar processing plants and much chemical and engineering research has been, and is being, conducted by the companies which build by-product coke plants, by many iron and steel companies, in several universities, research institutes, Federal, Interstate Compact, and state and municipal agencies.

General Procedures in the By-Product Oven Carbonization of Coal

The coal as received from the mines is crushed and ground, and conveyed to large storage bins located above and usually at the end of the battery of ovens. From the bins the ground coal, commonly a blend of two or more different coals, flows into the hoppers of the charging larry or car, which moves on rails along the top of the battery to the oven which is to be charged. The end doors of the oven have been tightly closed, either by jam-luting with mud or by use of the more recently developed self-sealing doors. The coal drops into the oven through large diameter tubes or spouts on the bottom of the larry car, which are spaced to coincide with the round openings, usually three or four of them, in the top of the oven. After the coal is discharged into the oven, the larry car moves back to the coalbin. A long leveling bar is moved to and fro over the top of the coal to level the surface of the charge. The covers are replaced on the charging holes and the leveler door is closed and all are well sealed to prevent escape of gas. The lid on the standpipe, which has been open during the charging of the oven, is now closed and the volatilized products from the coal pass into the collecting main. The heating time in the ovens ranges from 12 to 18 hours, a temperature of around 1,000°C (1,832°F) is attained, and the coal is thoroughly carbonized.

The largest by-product coking plant in the world is that of the United States Steel Company located in Clairton, Pennsylvania. It has nearly 1,500 ovens, carbonizes approximately 30,000 tons of coal daily, and has complete by-product recovery equipment. The top of a battery of coke ovens is shown in Figure 11, and the coke side in Figure 12, as the red hot coke is being pushed out of an oven, through the coke guide and into the quenching car. After the coke has been pushed from the oven

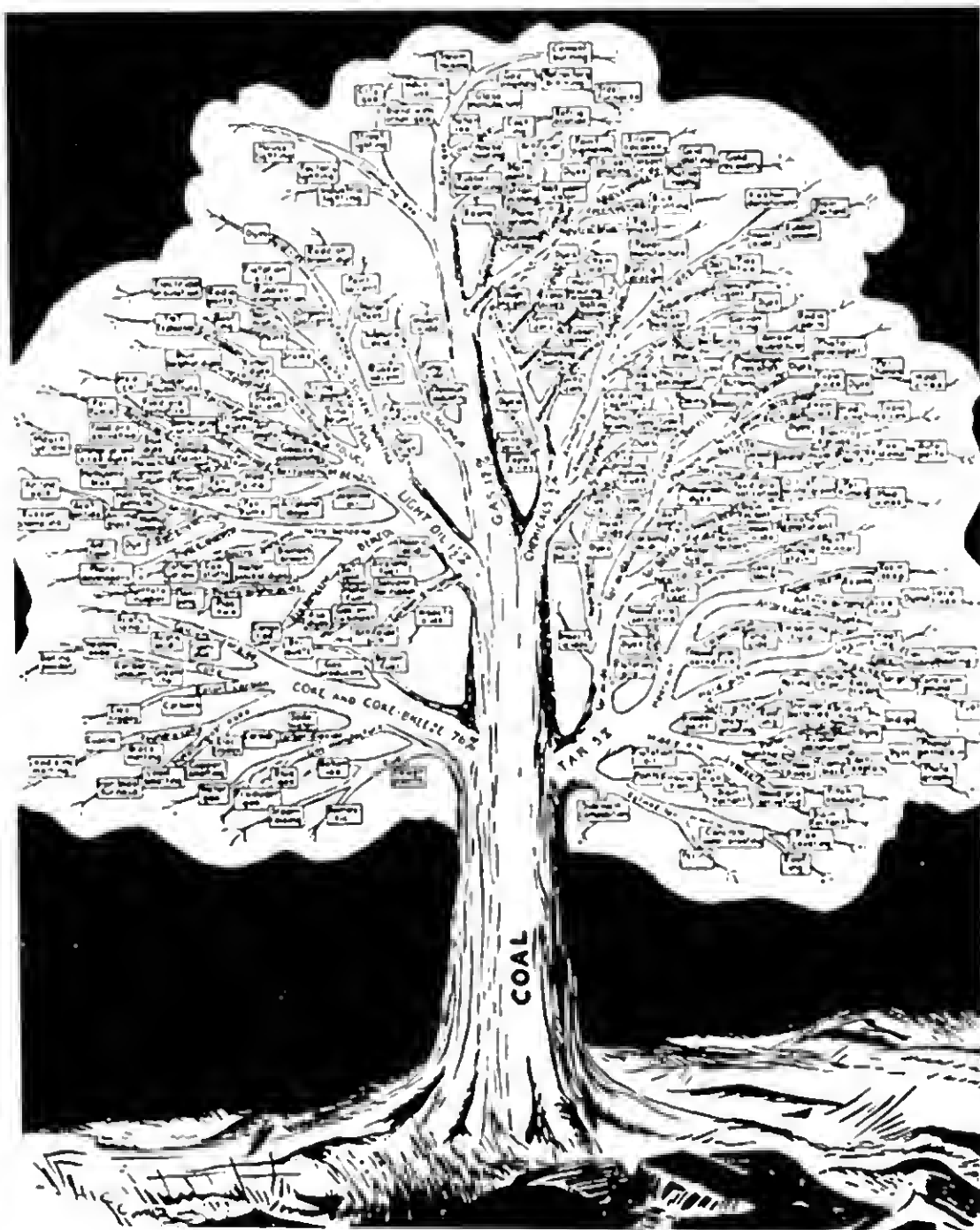


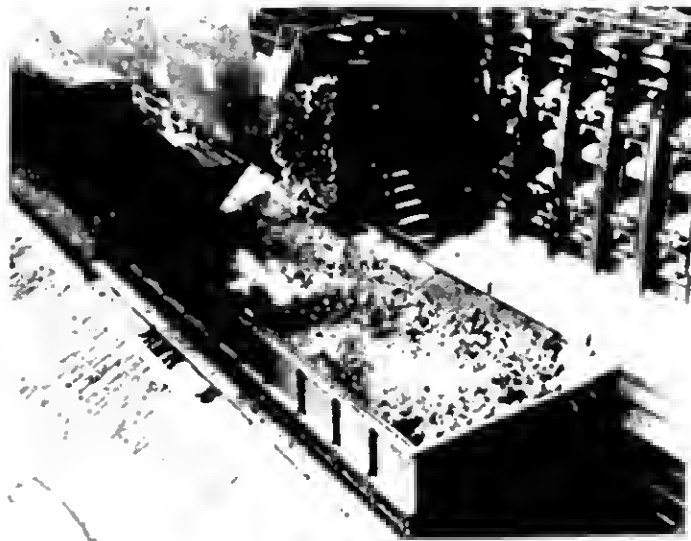
Figure 10. Coal products tree showing the primary products resulting from the retort carbonization of bituminous coal and a few of the hundreds of attainable by-products and derived compounds

the ram is withdrawn, the end doors of the oven are replaced, and the oven is made ready to receive the next charge of coal. The flaming coke in the quenching car is pushed over rails into the quenching station in



(Courtesy, Koppers Company, Inc.)

FIGURE 11. Top of a battery of by-product coke ovens showing larry car, covers over charging holes, and standpipes

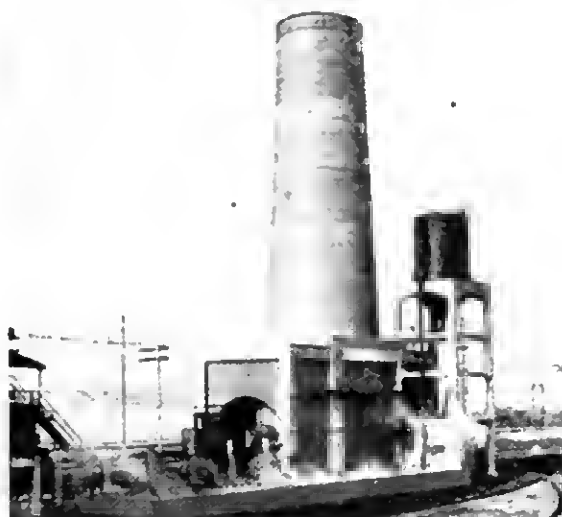


(Courtesy, National Tube Company)

FIGURE 12. Hot coke being pushed from coke oven into quenching car

which the coke is sprayed with about 4,000 to 5,000 gallons of water. A large cloud of steam pours forth from the top of the tower of the quenching station (Figure 13) as the coke is cooled below its ignition temperature. The quenching car with its load of steaming coke is drawn

to the coke wharf onto which the coke is discharged for further cooling. The coke falls from the wharf onto a large conveyor belt and is carried to the crushing and screening equipment where it is suitably sized for charging into blast furnaces, foundry cupolas, gas producers, or for household heating and other purposes. The surplus water sprayed on the coke drips into a sump below the quenching car and is reused. Make-up water is also pumped to the storage tank, usually constructed on the side of the tower at a sufficient height so that the water flows by gravity



(Courtesy, Koppers Company, Inc.)

FIGURE 13. Coke quenching tower showing water tank at the side and clouds of steam being emitted from top of stack

through the sprays and onto the hot coke. In some coke plants the phenolic waste liquors are utilized for make-up water but, as explained later, there are objections to this practice. In several plants dry-quenching processes have been installed to recover most of the heat in the hot coke. This method may give greater over-all thermal efficiency, but it is reported to be rather expensive, and has not been generally installed in coke plants in the United States. In some gas works, especially in Great Britain, much of the coke produced is used in different types of gas producers to make more fuel gases; this is called a complete coal gasification process. The procedures thus far should not cause any appreciable stream pollution. The comparatively small amount of air pollution has in recent years been reduced by using newer type larry cars which have closed hoppers and sleeve spouts with flanges which fit closely over the rims of the charging holes in the tops of the coke ovens, and by the use of steam jets in the standpipes while the ovens are being charged, and by the use of self-sealing oven doors. It would be practically impossible

to eliminate all coal and coke dust, and smoke from the atmosphere in an operating coke plant, but investigations are being made to reduce so far as possible air pollution in and around by-product coke plants.

PROCESSES FOR THE RECOVERY OF THE MORE IMPORTANT BY-PRODUCTS
OBTAINED FROM THE CARBONIZATION OF COAL IN BY-PRODUCT
COKE OVEN PLANTS AND CITY GASWORKS

The development through chemical and engineering researches of processes for the recovery of usable by-products has greatly reduced the water pollution which occurred at some plants during the pioneering years of the retort carbonization of coal. The researches were carried on usually for two principal purposes: (1) to abate water and air pollution and (2) to obtain commercial by-products, the revenue from which would help to offset the costs of the necessary unit operations required to recover the coal-chemical materials, as shown in Table 9. Processes were soon developed for the separation and recovery from the volatilized materials of the coal tar, ammonia, and crude light oils. The coke and gas were considered to be the main products and the other three materials, the primary by-products obtained from the high temperature, about 1,000°C or 1,832°F, carbonization of bituminous coal. On the weight and volume basis, Eldridge,⁶⁻² Lowy,¹³⁷ and the Ohio River Pollution Control Report,^{160a} give the following data as average yields per ton of coal carbonized in by-product ovens:

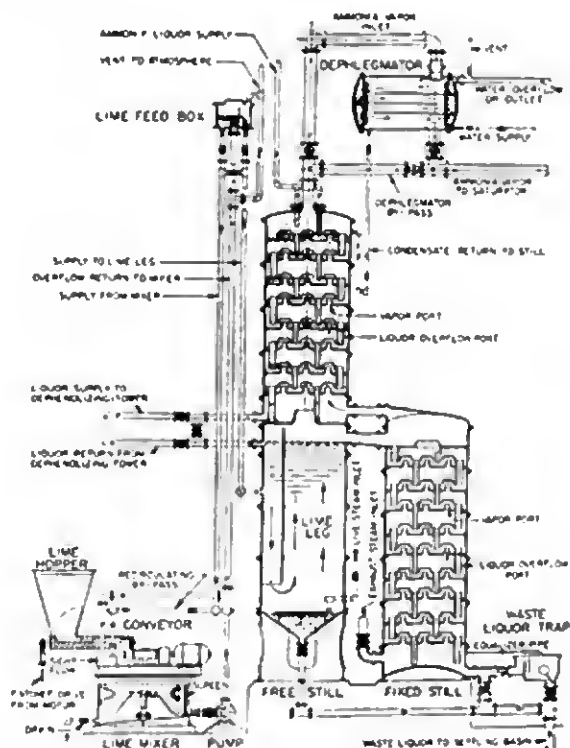
Product	Eldridge	Lowy	Ohio River Pollution Control
Coke (lb)	1,400	1,200 to 1,500	1,300 to 1,525
Coke breeze (lb)	68 to 100
Gas (cu ft)	11,000 to 13,000	11,000	10,300 to 11,300
Tar	9 to 13 gal	70 to 120 lb	5 to 12 gal
Ammonia (lb)	5 to 6	2 to 6	...
Ammonia as ammonium sulfate (lb)	24	...	17 to 26
Light oils (gal)	3 to 4	3 to 4	2.7 to 3.06

The approximate average volumes of wastes from various sources in by-product coke plants have been summarized as follows:^{160a}

Waste	Gal./ton of Coal Carbonized	5-Day BOD, 20°C, ppm	Phenol (ppm)	Cyanide (ppm)
<i>Water carrying waste products:</i>				
Ammonia still	22	3,974	2,057	110
Final cooler	315	218	105	...
Final cooler closed recirculating system	...	3,165	1,645	145 as KCN
Benzol carrying	15	647	72	...
Spent caustic	small

of by-products and derived compounds obtained from the carbonization of coal and of a few of their hundreds of uses.

The usual sequence of unit operations and processes by which the primary and some of the minor by-products are recovered from the substances volatilized when the coal is carbonized are shown in Figure 14, which is a general flow sheet for gas purification and conditioning.^{G-23} Most of the coal tar is separated from the gas and the aqueous ammonia liquor in the decanter and primary cooler, and the final traces of minute particles of tar, often as a tar-fog or mist, are removed by passing the gas stream through a "P and A" or other type of tar separator, or in the more recently built coke plants, by use of electrostatic equipment, such as the Koppers Elex, or the Cottrell precipitators, which remove from 95 to 99 per cent of the fine particles of tar from the mist. The recovered tar is usually shipped from the coke works to a tar products plant for processing and utilization.



(Courtesy, "Chemistry of Coal Utilization,"
edited by H. H. Lowry, published by John
Wiley & Sons, Inc., N.Y.)

FIGURE 15. Diagram of an ammonia still

Recovery of the Ammonia

The free ammonia in the gas and the ammonia liberated from the free and fixed ammonium compounds in the ammoniacal liquors by treatment in the ammonia still (Figure 15) are recovered, usually by the semidirect

process (Figure 16) as ammonium sulfate, by bubbling the gas through a dilute sulfuric acid solution in the saturator. The crystals of ammonium sulfate are separated from the acid solution by "whizzing" in large

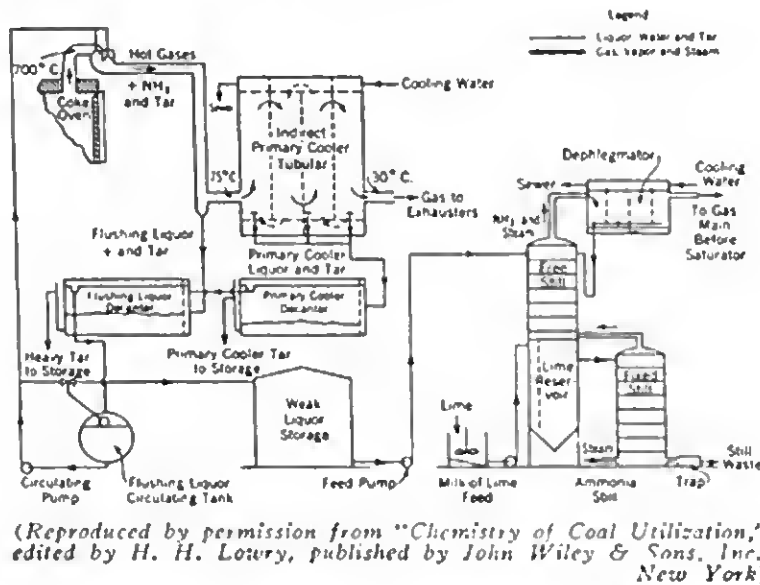
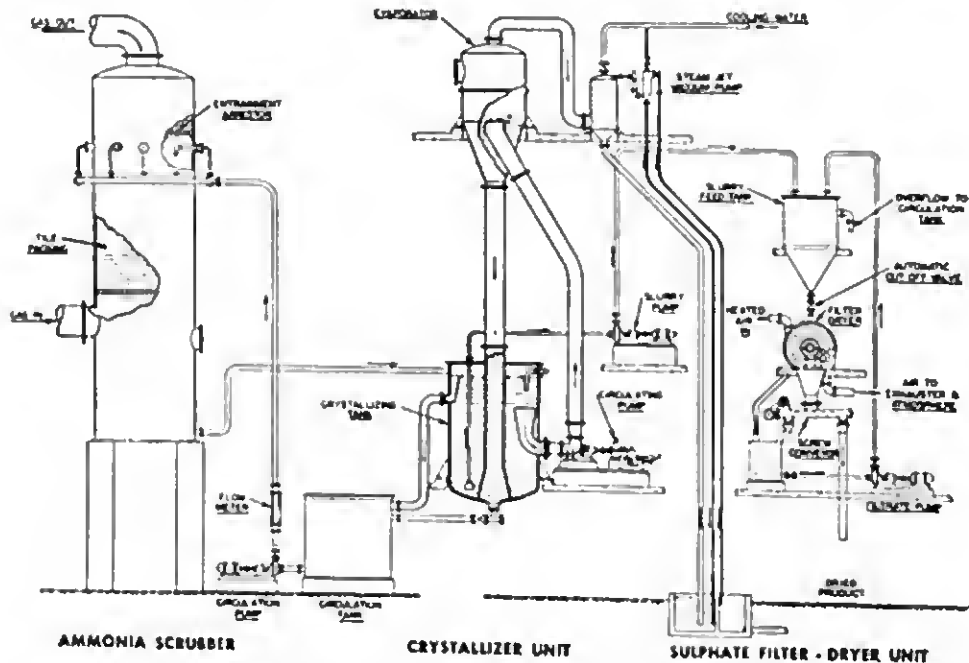


FIGURE 16. Flow sheet of the liquor circulation in a semidirect plant



(Courtesy, Wilputte Coke Oven Division, Allied Chemical & Dye Corporation)

FIGURE 17. Wilputte ammonium sulfate crystal process

basket centrifugals, and are sometimes further dried in rotary dryers. A process for making ammonium sulfate and using filter dryers is shown in Figure 17. Several patents have been granted for processes in which

the ammonia waste liquors or the raw ammonia gas would be reacted with waste pickle liquor from nearby steel mills to produce ammonium sulfate and iron oxide. Brief reviews of eight of these proposed processes were given by Hodge.^{100a} Since 1939 further researches along this line have been conducted by Hoak,⁹⁹ Tiddy,²¹⁴ Francis,⁷⁶ and others. As yet there are no industrial installations of this type of process, but investigations are still in progress. Ammonium sulfate is widely used as a nitrogenous fertilizer. In a few gas works and coke plants the ammonia is recovered as a concentrated aqueous solution of ammonium hydroxide, as the first product in the indirect process. If desired, the ammonia in the concentrated liquor may be volatilized and passed through the saturator to manufacture ammonium sulfate, which would complete the indirect process. In one or two plants in the United States, ammonia and phenols in the volatile products from carbonizing the coal are discharged to the atmosphere by applying a modified steam distillation. Research on the problem was cooperatively conducted by Hodge and Herndon,¹⁰³ and an industrial process was developed by Moses and Maekey.¹⁴⁸ The process is said to require considerable quantities of steam, and any serious air pollution would have to be avoided, but none has been reported at one installation of the process.

Compositions, Oxygen Demand Values, and Toxicities of Ammonia Liquors and Constituents. The compositions of the different kinds of ammonia liquors in gasworks and by-product coking plants are given in Tables 10, 11, 12, and 13.

TABLE 10. COMPOSITION OF CRUDE AMMONIA LIQUORS^{G-25}

	Plant A*	Plant B†
Ammonia, total	219 gpl	22.47%
Free	219 gpl	22.20%
Sulfide as H_2S	19.3 gpl	53.3 gpl
Pyridine bases as C_5H_5N	...	2.79 gpl
Phenols as C_6H_5OH	4.28 gpl	...
Oxygen absorption	39,110 ppm (4 hr at 27°C)	103,300 cc N/50 KMnO ₄ per liter
Specific gravity	...	1.055

*A. Key, "Gas Works Effluents and Ammonia," p. 18, The Institution of Gas Engineers, London, 1938.

†C. H. Stone, Proc. Am. Gas Assoc., 1923, 1159-1161. (Reproduced by permission from "Coal, Coke, and Coal Chemicals," by Wilson and Wells, published by McGraw-Hill Book Co., New York, 1950.)

A few analyses of ammoniacal liquors indicative of the compositions of such liquids obtained in gasworks practice in Great Britain are given in Table 13.

Several of the substances in the ammonia liquors have relatively high oxygen demands and a few of the constituents are toxic, even in

TABLE 11. TYPICAL COMPOSITIONS OF FLUSHING AND PRIMARY-COOLER LIQUORS^{G-25}

Liquor	Flushing (gpl)	Primary-cooler Condensate (gpl)
Total ammonia	4.20	6.94
"Free" ammonia	1.65	6.36
"Fixed" ammonia	2.55	0.58
Total sulfur	0.668	...
Sulfate as sulfur trioxide	0.212	...
Sulfide as hydrogen sulfide	0.003	...
Ammonium thiosulfate	0.229	0.29
Carbonate as carbon dioxide	0.374	...
Cyanide as hydrogen cyanide	0.002	...
Chloride as chlorine	8.13	1.05
Ammonium thiocyanate	0.82	...
Phenols	3.55	3.20

Reproduced by permission from "Coal, Coke, and Coal Chemicals," by P. J. Wilson, Jr., and J. H. Wells, published by McGraw-Hill Book Co., New York, 1950.

TABLE 12. COMPOSITIONS OF WEAK AMMONIA LIQUORS FROM SEVERAL COKE PLANTS^{G-11}

Plant	Ammonia-recovery Process			
	Semidirect A	B	Indirect C	D
Ammonia, total (gpl)	7.60	6.20	4.65	3.59
Free (gpl)	4.20	4.76	3.37	2.70
Fixed (gpl)	3.40	1.44	1.28	0.89
Carbon dioxide as CO ₂ (gpl)	2.35	3.94	2.78	1.74
Hydrogen sulfide as H ₂ S (gpl)	0.86	0.34	1.26	1.13
Thiosulfate as H ₂ S ₂ O ₃ (gpl)	0.022	0.51
Sulfite as H ₂ SO ₃ (gpl)	2.84
Sulfate as H ₂ SO ₄ (gpl)	...	0.15
Chloride as HCl (gpl)	6.75	1.85
Cyanide as HCN (gpl)	0.062	0.05
Thiocyanate as HCNS (gpl)	0.36	0.42
Ferrocyanide as (NH ₄) ₂ Fe(CN) ₆ (gpl)	0.014	0.039
Total sulfur (gpl)	1.014	0.57
Phenols as C ₆ H ₅ OH (gpl)	0.66	3.07
Pyridine bases as C ₅ H ₅ N (gpl)	0.48	0.16	1.27	0.98
Organic number, cc N/50 KMnO ₄ per liter	4,856	3,368

"Chemistry of Coal Utilization," p. 1380, ed. by H. H. Lowry, John Wiley & Sons, Inc., New York, 1945.

low concentrations, to fish and other forms of aquatic life. The effects of adding small quantities, 0.5 to 3 per cent of ammonia-still waste, to raw sewage were extensively investigated by Mohlman.¹⁴⁴ As shown

TABLE 13. AVERAGE COMPOSITIONS OF AMMONIACAL LIQUORS FROM CARBONIZATION OF COAL IN DIFFERENT TYPES OF RETORTS¹⁵⁵

Constituent	Intermittent Vertical Retorts			C.V.R.* Yorks Coal	C.V.R.*	Hori- zontal Retorts
	Retort House	Con- denser Liquor	Scrub- ber Liquor			
<i>Grams per 100 cubic centimeters</i>						
Free NH ₃	0.41	2.10	3.81	1.34	1.00†	1.50†
Fixed NH ₃	1.62	0.13	0.08	0.34	0.33	0.50
Sulfides as H ₂ S	0.02	0.50	0.84	0.263	0.15	0.25
Thiosulfate as S	0.19	0.03	0.03	0.051	0.10	0.10
Thiocyanate as CNS	0.31	0.07	0.06	0.194	0.20	0.20
Chloride as HCl	2.29	0.18	0.26
Carbonate as CO ₂	14.1	1.92	3.61
Phenol as C ₆ H ₅ OH	0.35	0.47	0.05	0.392	0.35	0.25

Oxygen adsorption; parts per 100,000 due to:

Sulfide	24	667	1,130	354	200	336
Phenols	619	839	80	698	620	445
Thiosulfate	164	29	27	44	85	85
Thiocyanate	254	55	51	160	165	165
Difference	589	318	285	265	580	160
Total	1,650	1,902	1,573	1,521	1,650	1,191

*C.V.R., Continuous Vertical Retorts.

†From A. Key,^{G-9}

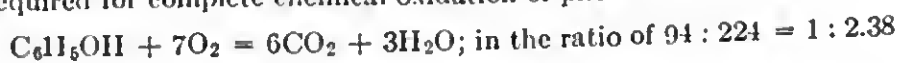
T. Nicklin, Courtesy, *Gas World*, 128, 300-3 (Feb. 21, 1948).

TABLE 14. EFFECTS OF ADDITIONS OF AMMONIA-STILL WASTE ON THE BIOCHEMICAL OXYGEN DEMAND (BOD) AND OXYGEN CONSUMED (OC) VALUES OF MUNICIPAL SEWAGE¹⁴⁴

Raw Sewage (R.S.) + Per Cent Still-Waste (S.W.)	BOD		O.C., KMnO ₄ Method	Phenol Calcd.	ppm BOD per ppm Phenol		Bacterial Count, Agar, 48-hr
	5-day	10-day			5-day	10-day	
Raw sewage	110	120	25.0	0.02	343,000
R.S. + ½% S.W.	136	170	58.8	14.5	380,000
R.S. + 1% S.W.	165	210	125.0	28.9	1.90	3.11	880,000
R.S. + 2% S.W.	200	225	181.0	57.8	1.56	1.82	880,000
R.S. + 3% S.W.	247	310	234.0	86.7	1.58	2.19	289,000
(Avg.					1.68	2.37)	

Ammonia—S.W. used contained 2,886 ppm of phenol.

Oxygen required for complete chemical oxidation of phenol.



Mohlman, F. W., *Am. J. Pub. Health*, 19, 145-156 (1929).

TABLE 15. OXYGEN ABSORBED BY VARIOUS CONSTITUENTS IN GASWORKS WASTE LIQUORS¹⁴⁰

Constituent	Oxidation Reaction	Theor. Oxygen Requirement	O/A g/g of Constituents Found by KMnO ₄ Test, 4 Hours at 26.7°C	Found % of Theor.
Sulfide	$\text{H}_2\text{S} + 2\text{O}_2 \longrightarrow \text{H}_2\text{SO}_4$	1.882	1.345	71.5
Phenol	$\text{C}_6\text{H}_5\text{OH} + 7\text{O}_2 \longrightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$	2.382	1.780	74.8
Cresol	$\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{OH} + 17\text{O} \longrightarrow 7\text{CO}_2 + 4\text{H}_2\text{O}$	2.519	1.540	61.1
Catechol (-O)	$\text{C}_6\text{H}_4(\text{OH})_2 + 7\text{O}_2 \longrightarrow 6\text{CO}_2 + 3\text{H}_2\text{O}$	1.891	1.245	65.8
Thiocyanate (as CNS)	$\text{NH}_4\cdot\text{CNS} + 2\text{H}_2\text{O} + 2\text{O}_2 \longrightarrow \text{CO}_2 + (\text{NH}_4)_2\text{SO}_4^*$	1.103	0.827	74.9
Thiosulfate (as S ₂)	$\text{H}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{O}_2 \longrightarrow 2\text{H}_2\text{SO}_4$	1.000	0.856	85.6

(A. Marsden, *The Gas World*, 133, No. 3487, 653-6 (1951)).

The O/A in p.p. 100,000 is calculated from the concentrations in grams/100 c.c.s. of the various constituents.

Sulfide concentration as $\text{H}_2\text{S} \times 1345$

Phenol concentration as $\text{C}_6\text{H}_5\text{OH} \times 1780$

Thiocyanate concentration as $\text{CNS} \times 827$

Thiosulfate concentration as $\text{S} \times 856$

*Frankland and Silvester give equation: $\text{CNS} + 3\text{O} \longrightarrow \text{SO}_3 + \text{CN}$.

in Table 14, the addition of 3 per cent of the still waste increased the 5-day biochemical oxygen demand (BOD) of the sewage from 110 to 247 ppm, and the oxygen consumed (OC) value from 25 to 234 ppm. The oxygen absorbed (O/A) by each of six of the substances occurring in gasworks waste liquors were reported by Marsden¹⁴⁰ to range from

TABLE 16. OXYGEN DEMANDS AND PHENOL CONTENTS OF SOME BY-PRODUCT COKING AND CHEMICAL PLANT WASTE LIQUORS

Plant	Sample		Parts Per Million (ppm)			
	No.	Description	OD	OC	5-day BOD	Phenol
A	1	dephenolizer feed liquor	4,930	...	2,040	790
	2	ammonia still waste	1,580	...	165	11
	3	ammonia still waste	2,770	2,300	315	17
B	1	dephenolized liquor; feed to ammonia still	2,530	1,850	800	28
C	1	ammonia liquor; still waste drain line	2,650	...	740	...
D	1	waste ammonia liquor from tower	...	2,420	...	293
E	1	over-all plant effluent	...	23.6	4.2	<0.42
	2	over-all plant effluent	...	32.8	10.8	0.42
	3	over-all plant effluent	...	26.4	9.0*	0.77
F	1	effluent from springing tar base sulfate	5,000	...	4,290	630
	2	composite from plant sewers	90	...	87	10
	3	composite from plant sewers	160	...	96	23
G	1	over-all plant effluent	...	250	205	42
H	1	aqueous effluent from oil-water separator at a chemical plant	...	1,770	3,800	...
I	1	chemical process neutral waste liquor	10,900	...	1,810	...
	2	composite sample of chemical plant waste liquors	...	3,200	1,160**	...

*D.O. depletion >70%.

**D.O. depletion <40%.

Hodge, W. W., and Tallon, G. R., Koppers Company's Effluents Treatments Fellowship, Mellon Institute.

61.1 to 85.6 per cent of their respective theoretical oxygen requirements (Table 15). The OD, OC, and 5-day BOD values of several by-product coke, tar processing, and chemical plant waste liquors were investigated by Hodge and Tallon, and are given in Table 16. The relative toxicity, O/A, and rate of biochemical oxidation of seven of the constituents in ammonia waste liquors, as given by Marsden,¹⁴⁰ are shown in Table 17. The fixed ammonia is the only constituent listed as nontoxic, three substances are highly toxic, two are low, and phenol is given as of

medium toxicity. The toxicity of ammonia-still wastes is probably due largely to the action of the chemical on the test-organism, but depletion of the dissolved oxygen in the liquors or solution used for the tests may also be a factor. Different kinds of fish, insects, and microorganisms vary widely in their respective tolerances to toxic materials. Brook trout and goldfish are considered to be more sensitive to toxic substances or

TABLE 17. RELATIVE TOXICITY AND OXYGEN ABSORPTION OF DIFFERENT CONSTITUENTS IN COKE AND GASWORKS WASTE LIQUORS¹⁴⁰

Constituent	Toxicity	Oxygen Absorption O/A*	Rate of Biochemical Oxidation	Remarks
Free ammonia	high	nil	very slow	*In comparison with these figures it may be noted that the O/A for domestic sewage varies from (say) 5 to 15 p.p. 100,000
Fixed ammonia	nil	nil	very slow	
Sulfide	high	1,345	fast	
Cyanide	high	600	very slow	
Thiosulfate	low	856	fast	
Phenol	medium	1,780	fast	
Higher tar acids	low	high	very slow	

Marsden, A., *Gas World*, 133, No. 3487, 653-6 (1951).

to unfavorable biological conditions in water bodies than other types of fish. The survival time of goldfish in water containing 10 ppm of phenol was found by Ellis⁶⁻³ to be 72 hours to over 4 days, and in water containing 1 ppm of phenol the survival time was over 4 days. There was no apparent injury to the fish in either experiment. Quite similar results were obtained by Bach.^{12,14}

Extensive investigations were carried on by Shelford and his associates¹⁸¹⁻⁴ of the Illinois State Laboratory of Natural History as to the toxicity of certain industrial wastes and organic compounds on fish. Most of the experiments were conducted using goldfish as the experimental organism. The results indicated that a number of the compounds occurring in the waste liquors from gasworks and by-product coke plants were toxic to fish but the toxicity varied over rather wide limits. They found that the fish reacted positively toward phenol solutions and instead of avoiding them they would swim toward points of higher phenol concentrations. This observation has since been verified by other investigators.

Possibly the most recent contribution to the toxicity of substances occurring in the carbonization plant effluents has been made by Nellist.¹⁵² He investigated the characteristics, compositions, and toxicities of coal-washery and coke-works effluents, and the toxicities of several of the compounds present in the waste liquors. He also estimated pollutional effects of the substances on a receiving watercourse. His

summary of the toxicity of a number of these substances is given in Table 18.

The very wide differences in the data published regarding the toxicities of various chemicals have recently been discussed and some of the reasons for the large variations are as follows: (1) the kind of fish or other organism used in the tests, (2) the temperature at which the experiments were conducted, and (3) the kind of water and other environment in which the organisms were placed during the experiments. Among the variables of the water factor are its salinity, pH value, alkalinity or acidity, hardness, and contents of dissolved oxygen and carbon dioxide. The toxicity of ammonium salts has been given by different authors in values ranging from 100 to 1,000 ppm. Apparently the data given on toxicity of chemicals and waste liquors must be considered in relation to the conditions under which the investigations were conducted.

TABLE 18. LIMITING CONCENTRATIONS OF SUBSTANCES TOXIC TO FISH¹⁵²

Substances	ppm
Sulfides (as/S) and H ₂ S	1.0
Cyanide (as/CN)	0.3
Phenol and cresols	5.0
Higher tar acids	10.0
Naphthalene	10.0
Ammonium thiocyanate	200.0
Ammonium thiocyanate (as NH ₃)	45.0
Ammonium sulfate (as NH ₃)	262.0
Ammonium chloride (as NH ₃)	194.0
Ammonium carbonate (as NH ₃)	35.0
Free ammonia (i.e., NH ₄ OH)	10.0
pH value, "safe range"	5.0 to 9.0

Nellist, G. R., *Gas World*, 135, No. 3516, Supplement, 7-13 (Jan. 5, 1952).

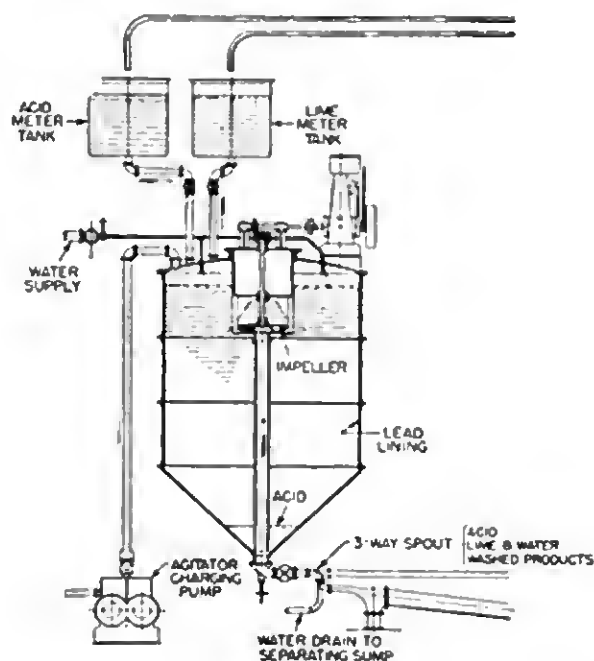
The concentrations of eight of the materials usually present in waste ammonia liquors, which may be toxic to fish, are given by Gollmar,^{79a} and Coxon⁴⁷, in ppm, as follows:

Phenols	10	Thiocyanate	200
Higher tar acids (catechol)	10	Cyanide	10
Ammonia (free NH ₄ OH)	10	Pyridine	400
Ammonium salts	500	Naphthalene	5

Three additional groups of waste substances resulting from the very necessary by-product coal-coking operations, not listed in the toxicity tables, but which do require special processing to avoid air and/or stream

pollution, are as follows: (1) the acid sludge from the purification of the light oils; (2) the sulfides, especially hydrogen sulfide; and (3) miscellaneous oily wastes.

Disposal of the Acid Sludge. After the ammonia has been removed from the coal gas it flows through a cooling tower and then up through countercurrent flowing, recirculated, absorption oil, which strips the



(Courtesy, United States Steel)

FIGURE 18. Diagram of an agitator for acid washing of light oil

aromatic light oils containing benzene, toluene, xylene and related compounds from the gas. The benzolized absorption oil flows from the bottom of the extraction column to a steam still in which the crude light oils are separated from the benzolized oil. The debenzolized-absorption oil is pumped to the top of the extraction column for reuse. The crude light oils are subjected to: first, a wash with 66° or 60° Baumé, sulfuric acid in a lead-lined agitator; second, an alkaline wash, usually with lime slurry; and third, a water rinse.⁶⁻²³ The sludges and the wash waters in turn settle into the cone-shaped bottom of the agitator and are drawn off for proper waste disposal (Figure 18). After removal of water in the water separating sumps, the partially purified light oil may be used or sold, but it is usually further purified by steam distillation and may be fractionally distilled into commercial benzene, toluene, xylene, or different grades of solvent naphthas.

The treatment and disposal of the spent acid or sludge resulting from washing the crude light oil has for many years been a serious waste

disposal problem at many gasworks and by-product coke plants. Considerable research on the problem has been done and several different methods have been devised for the treatment and disposal of the acid sludge in order to avoid stream or air pollution. The methods may be classified as follows: (1) dumping; (2) burning; (3) washing; and (4) modifications in the procedures for washing the light oil.

Dumping. In the early days, and to some extent at the present time, the acid sludge is dumped into pits in the earth or lagoons, or, where the coke plant is integrated with an iron and steel mill, then the sludge may be emptied onto piles of hot furnace slag, which is a combination of dumping and burning. The objections to the open-pit method of disposal are that the acid sludge renders the soil in the pit, and adjacent to it, unusable for agricultural purposes and the acid condition would be injurious to foundations of buildings. The sludge ponds fill up and new ones have to be prepared. The practice of burning off the surface oil from the acid sludge may cause objectionable air pollution, and if the oil is not burned off it is a constant fire hazard. The sludge may be drawn from the oil washer into a specially built sludge car or tank truck. Slag ladle cars have been used to convey the acid sludge to the dump. A further objection to this method is that heavy rains may wash the acid and oil into a nearby waterway and thus cause objectionable stream pollution. With increased legislation against air and stream pollution the trend has been away from the practice of simply dumping the sludge into pits or sludge lagoons.

Burning. Since the burning off of oil from the sludge pits has such objectionable features, considerable research has been applied to the design and construction of furnaces in which the acid sludge could be burned to an ash without the emission of objectionable smoke and fumes. In some gasworks and coke plants a method of burning the acid sludge along with the fuel used in heating the boilers has been practiced. The combustion of any sulfur-containing fuel which produces large percentages of sulfur dioxide in the flue gases is objected to because of the corrosive action on the boiler tubes and drums caused by the sulfur dioxide. However, Preston¹⁶⁹ has calculated that the sulfur dioxide produced from complete combustion of all the acid sludge formed by washing 3.5 gal of light oil per ton of coal carbonized, and applying 0.4 lb sulfuric acid per gal of light oil would amount to only about 20 per cent of the sulfur dioxide present in the stack gases of a battery of coke ovens which was burning coke oven gas containing 400 grains of hydrogen sulfide per 100 cu. ft. If the residual free acid was first removed from the sludge and only the acid-tar layer was burned, the sulfur dioxide in the stack gases would be increased by only about 2 per cent.

In the latter case the waste gases from the burning of the sludge could easily be taken care of in the coke oven stack. If the sludge is too viscous to flow through ordinary burners, it may be diluted with sufficient coal tar so that the sludge flows readily. Several types of sludge burning furnaces have been proposed, a few of them patented and put into practical operation. Some types are of a vertical hearth construction; others horizontal; and, recently, Maurer and Roberts¹⁴² have patented a continuous rotary kiln provided with means for feeding in the acid sludge, controlling the temperature during operation, and for removing the product.

Washing. The acid sludge may be separated into two or more layers by treatment with steam in open pots; old slag ladle cars are reported to have been used at some plants, or semi-closed stills with equipment for recovering the light oil evolved on heating. On treatment with open steam a pitchy, hydrocarbon mass forms the bottom layer, the next layer is dilute sulfuric acid, and the top layer may be a light oil. The light oil may be recovered by skimming or distillation and the middle layer may contain sulfuric acid of 35 to 45 per cent concentration, which is frequently used in the saturators manufacturing ammonium sulfate. This dilute acid may be rather dark-colored but, by proper handling, it will produce a salable ammonium sulfate. A process of this type was patented by Thompson²¹² and the equipment for its operation was built by H. Koppers Company over thirty years ago, and is reported to be still operating. A process developed in England by Stevenson¹⁹⁹ has also had practical application. In the Stevenson Process, particular attention is given to the distribution of the steam through the sludge and some ammonia gas is introduced into the head of the still to break down the foam. In the Simonsen-Mantius process the sludge is boiled for several hours by heating it with direct steam. In this process some light oil is recovered from the evolved vapors. The acid recovered is of about 50 per cent concentration and is sufficiently pure for use in the saturators to make ammonium sulfate or other fertilizers. By this and some other processes, from 20 to 70 per cent of the sulfuric acid used to wash the light oil may be recovered. Some processes have used alkalies to neutralize the acid, but this has not become common practice.

Modifications in the Procedures for Washing the Light Oil. Treatment of the light oil with other acids such as phosphoric, sulfonic, or hydrochloric; or with concentrated solutions of aluminum chloride, zinc chloride; and with different oxidizing agents such as ozone, or potassium permanganate, and many other substances, have been proposed. However, the treatment of the light oil with concentrated sulfuric acid either 60° or 66° Baumé is almost universal practice. This acid has advantages

of relatively low cost; it removes nearly all of the sulfur compounds and the operations are simple to apply.

One of the more widely used modifications of the formerly common washing procedures is the Ufer Process which was described by Phillips¹⁶³ and Preston¹⁶⁹ and installations were introduced by the Koppers Construction Company in 1931. By this process the formation of a difficult-to-handle acid sludge is reduced or eliminated by hydrolysis. The resins in the oil layer separate after the acid washing and before any sludge is drained off. A quantity of water equal to about twice the volume of the original acid applied to the light oil is added to the washer. The acid layer contains some dissolved materials. It is drained off and is usually satisfactory, even though reddish-to-purple color, for use in the saturators to make ammonium sulfate. Some modifications have been made in the original Ufer Process by which the crude light oil is first washed with a used acid and the batch "Uferized" with water. The use of a slightly diluted acid forms a sludge which readily hydrolyzes and completely dissolves in the oil. A distillation procedure is applied which separates the heavy ends of the oil that contain most of the resins. The resulting oil is washed again with fresh 66° Baumé acid and, because of the previous washing, no insoluble sludge is formed. The recovered acid is then used for the main wash of another batch of crude light oil. The "Uferized" acid is used in the ammonia saturators. This modification of the Ufer Process eliminates the undesirable features of the original Ufer Process, in that the oil is finally treated with 66° Baumé acid. By using this process about 90 per cent of the acid used can be recovered and from 1 to 4 per cent of light oil.

Another modification of the oil washing operation is the Instill Process proposed in Germany which would apply some adsorbent earth containing ferric sulfate together with some sulfuric acid. The Silica-Gel Process has been used to adsorb the gum-forming substances in the light oil, and many other modifications of processes for acid washing of the crude light oil have been proposed but they do not appear to have received wide acceptance in the industries.

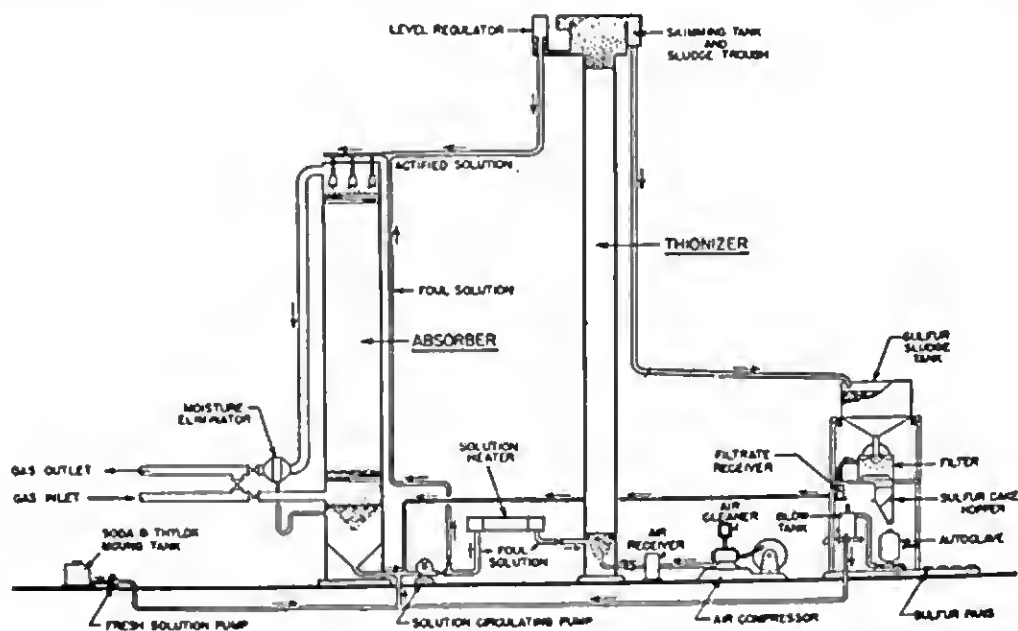
In common with the petroleum refining industry, the coal carbonization industry has had for many years this problem of treatment and disposal of acid sludges. Preston¹⁶⁹ states that a patent was granted in the United States in the year 1859 in connection with the Petroleum Industry for a process of separating sludge from the acid and concentrating the acid for reuse. From that time to the present, investigations and researches have been and are still being carried on to develop a better process for removing the impurities from the crude light oil and for obtaining useful by-products from the residual sludge after the oil

and acid have been removed from it. It is known that there are considerable amounts of heavy hydrocarbons remaining in the pitch, and research is presently directed toward recovering some of these compounds in commercial forms and quantities

Processes for the Recovery of Hydrogen Sulfide

This compound is highly toxic and if allowed to escape might cause dangerous air pollution, and if absorbed in wash water and the solution discharged to waterways, it would be inimical to aquatic life. Fortunately, methods were quickly developed by the gas production industries for removal, and later recovery and utilization, of the hydrogen sulfide evolved when coal is carbonized. That portion, commonly about one-third of the coal gas produced, which is used to heat the coke ovens, does not require further purification after the light oils are removed. If the coke ovens are heated with blast furnace or producer gas, then all the coal gas made is subjected to further purification as shown in Figure 14. In the early years of the industry and in some plants today, especially in several European countries, the hydrogen sulfide was and is removed from the gas by passing it through or over layers of iron oxides, usually mixed with wood shavings or other spacing-materials, which are spread on trays or shelves enclosed in large steel oxide boxes. In some plants the spent oxide is a waste material and is disposed of in pits or piles, so located that the runoff after rains will not contaminate adjacent streams. In other plants the spent oxide is revived by calcining, the recovered oxide is reused and the evolved sulfur dioxide is used in the manufacture of sulfuric acid. Great progress has been made during the past twenty years in developing improved processes for the recovery of hydrogen sulfide from the gases produced in by-product coke plants, city gas works, oil refineries, and some other industries. Among these liquid purification processes are the following: Improved Ammonia,¹⁶⁵ Alkazid,¹⁴⁶ Auto,¹⁴⁶ Borate,²⁵ Espenhahn,¹⁶⁵ Ferrox,¹⁹⁷ Girbotol,¹⁴⁶ Girdler,^{23,24} Houdry,¹⁶⁵ Koppers vacuum actification,^{80,118} Magnesium hydroxide,¹⁹⁴ Nickel,¹⁶⁵ Phenolate,^{37a,166,179} Phosphate,^{174a} Seaboard,^{58,196} Thylox,^{57,79,113,164a} and there are others. A number of these processes have been described by Powell¹⁶⁵ and several others by Monkhouse.¹⁴⁶ Most of the processes recover the hydrogen sulfide as such, but some produce elemental sulfur. In either form the recovered material is largely used in the manufacture of sulfuric acid. One process of each general type is briefly described. In the Thylox process (Figure 19), as described by Denig,⁵⁷ Jacobson,¹¹³ Powell,^{164a} and Gollmar,⁷⁹ the hydrogen sulfide in the gas is absorbed in a clear, slightly alkaline solution of sodium thioarsenate containing less than 1 per cent equivalent

of arsenic trioxide. The absorbed hydrogen sulfide is decomposed by blowing air through the containing liquid; the sulfur is separated in a very finely divided form, and the arsenate solution is reactivated. Some replacements of losses of soda ash or ammonia to maintain the proper pH, 7.5 to 8.0, and of the arsenic compounds are necessary to maintain the high efficiency of hydrogen sulfide removal, which ordinarily is about 98 per cent, but can be operated for complete removal where that is necessary. The very finely divided sulfur, much of it being less than 3 microns in diameter, is widely used as a dusting insecticide or fungicide



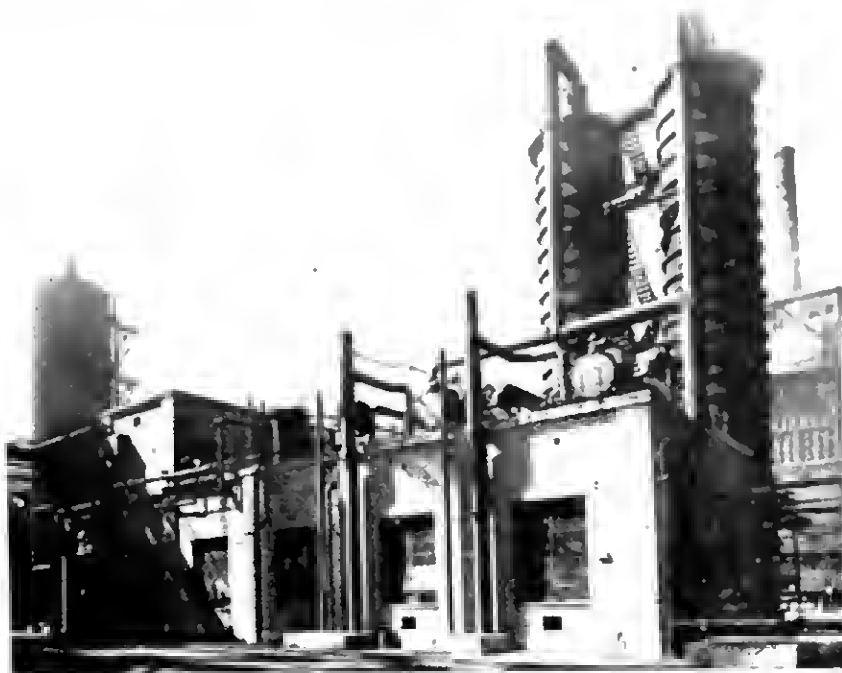
(Courtesy, Koppers Company, Inc.)

FIGURE 19. Flow diagram of Thylox Process for recovery of H_2S from coal gas

and in crop protective agricultural sprays. The sulfur may be melted into sticks or lumps, and also used to make sulfuric acid. In the Koppers vacuum actification process (Figure 20), as described by Gollmar,⁸⁰ and by Kastens and Barraclough,¹¹⁸ both the hydrogen sulfide and the hydrogen cyanide are removed from the gas. The hydrogen sulfide may be sold, or used to manufacture sulfuric acid. The hydrogen cyanide may be converted to sodium cyanide, widely used in some metallurgical industries, or may be converted into other commercial products, such as ferrocyanides or thiocyanates. The present world shortage of sulfur has focused efforts to recover more by-product sulfur. The many installations of the different processes previously listed, recover, annually, from the by-product coke plants in the United States, the equivalent of about 7,000,000 lb of available sulfur for the production of sulfuric acid and other useful materials. Many millions more pounds of the hydrogen

sulfide, which otherwise might cause air or stream pollution, are recovered by certain of these processes from oil refinery gases and are converted into useful products.

Disposal of Oily Wastes. Increased attention is being given by the coal carbonization companies to the careful disposal of any oily wastes and

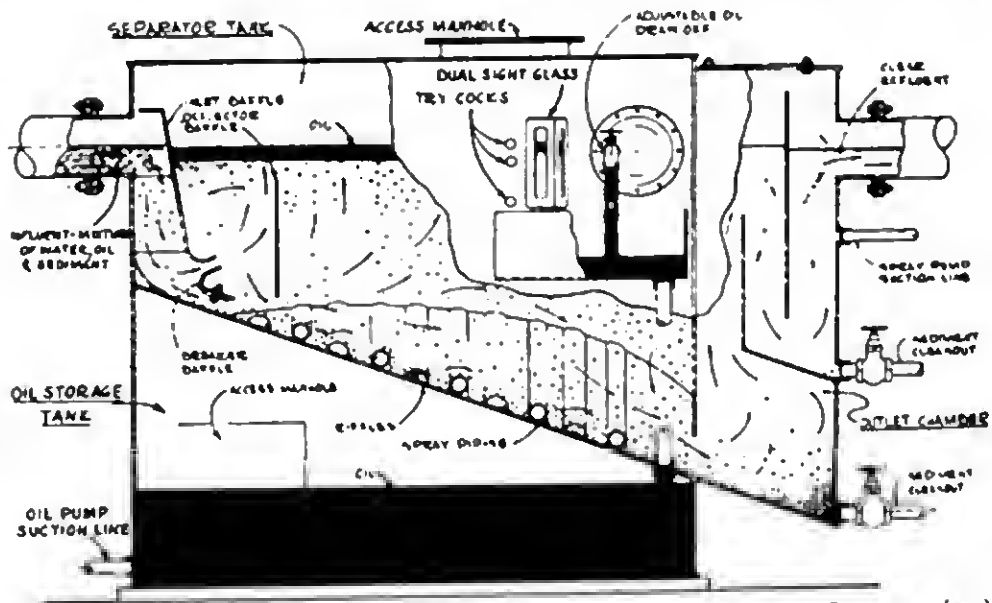


(Courtesy, Koppers Company, Inc.)

FIGURE 20. Installation of vacuum hot-actification process for recovery of HCN and H_2S from coke oven gas

greases so that they do not enter the sewers or drainage channels and cause water pollution. Experiments have shown that films of oil only 0.0000030 inch in thickness cause a silvery sheen on the surface of water; bright bands of color, iridescence, are visible when the oil film reaches a thickness of about 0.0000120 inch; and when the film has a thickness of 0.0000800 inch the colors are much darker and might attract less general attention than do the very thin, highly iridescent films of oil.¹ Thick films of oil on water constitute a fire hazard, and even thin films of oil, while they may not be seriously dangerous to human health, do create unfavorable conditions for the propagation of aquatic organisms, may impart oily flavors to fish, unpleasant tastes and odors to water supplies, are obnoxious on recreational beaches, and since they are easily seen they frequently are the cause of complaints to governmental regulatory agencies. The gas production industries have found the experiences and publications¹ of the petroleum industry helpful in their efforts to combat oil pollution of waterways. The usual designs for

oil-water separators in petroleum refineries may have to be somewhat modified for the oily wastes around gas and coke plants, since they may contain small amounts of tar oils, but the fundamental principles for construction and operation of the gravity type separators are quite similar. To remove the last traces of oils, installations of coke, sand, or hay filters, and of surface skimmers have proved to be useful. At one large refinery, as described by Giles, Scheinemen, Nicholson, and Austin,⁷⁸ the effluent from the oil-water separator is treated with ferrous sulfate and lime to form a floe which occludes the fine oil particles, and these are removed from the water by sedimentation and filtration. The oil content of the final effluent is below the specification set by the State Water Control Agency. Oil-water separators have been installed



(Courtesy, Gale Oil Separator Company, Inc.)

FIGURE 21. Gale water, oil, tar, and grease separator

at some by-product coke plants and city gasworks. Coke filters for the removal of oily wastes are, naturally, used at many such plants, while hay filters are used at a few plants. The quantities of the oily wastes can often be greatly reduced by improved housekeeping in the plants. Oil-water separators may be designed and construction supervised by the company engineers or may be purchased from companies specializing in that type of equipment. A longitudinal, elevation diagram of a Gale separator, similar to several small and some large installations in the United States, is shown in Figure 21, and a Morse separator (water-tar-oil) installed at a large gasworks in England is illustrated in Figure 22. Investigations are needed to develop reasonably priced water-oil-tar separators which will skim off the light surface floating

oils and also remove the heavier petroleum and tar oils from the waste waters so that the oil contents of the plant effluent will be below the limits set by government pollution control agencies and do so without the additional costs involved in applying post-separator processes.

The installation of a "well-point" system for recovering oil which has leaked into the ground at a large by-product coke plant was described by Koons¹²² at the meeting of the Production and Chemical Divisions

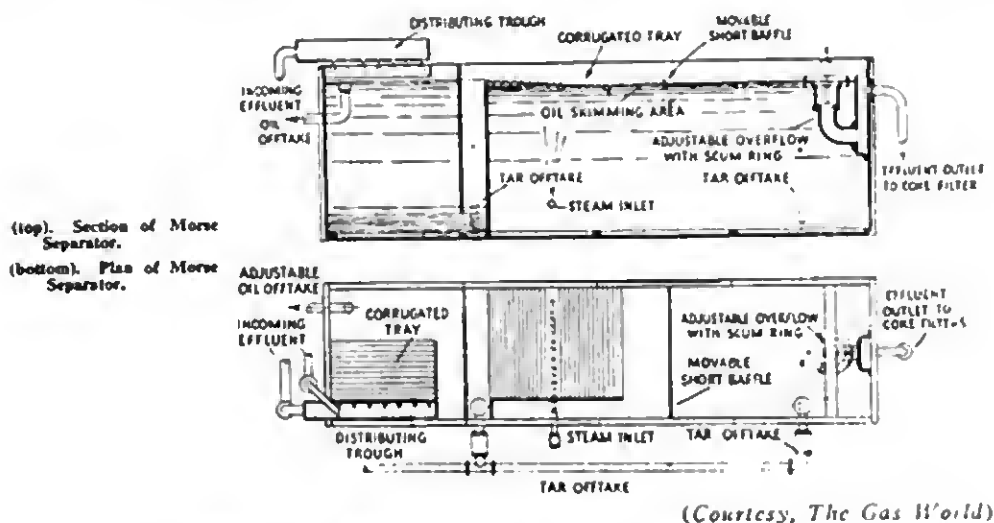


FIGURE 22. Morse water, tar, and oil separator¹⁴⁰

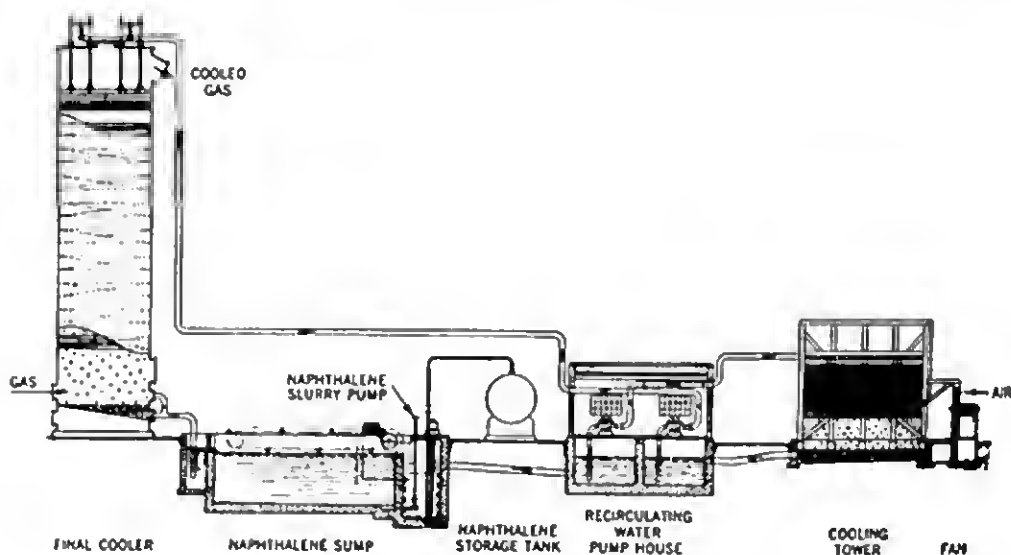
of the American Gas Association in May 1952. This is believed to be the first installation at a by-product coke plant in the United States of such a system for recovering oil which has soaked into the plant site or escaped into it from leaks in the pipelines. The objective of this installation was primarily to prevent oil seepage into the adjacent watercourse. However, a considerable quantity of usable oil was recovered. The "well-point" system has been used for similar purposes at a few petroleum refineries, and considerable amounts of usable oil have been recovered.

Naphthalene and Anthracene Recovery

Naphthalene is among the more toxic substances present in the volatilized products from coke plant and gasworks operations. It is only slightly soluble in water at low temperatures and this property is applied in its separation and recovery. Much of the naphthalene separates in the sump following the final cooler (Figure 23). The small amount of naphthalene still remaining in the gas is largely removed by absorption in a light, low viscosity fraction from petroleum, which flows counter-current to the ascending gas in a scrubbing tower especially designed

by the Koppers Company for the purpose. Crude naphthalene is also recovered from carbolic oil after the tar acids and pyridine have been removed by chilling the oil in crystallizing pans. The naphthalene crystals are separated from the oil by centrifuging. The naphthalene may then be purified by sublimation or distillation.

The crude naphthalene obtained during 1948 from by-product coke plants amounted to 105,816,670 pounds, and much more naphthalene



(Courtesy, Koppers Company, Inc.)

FIGURE 23. Naphthalene recovery in a final cooler system

was recovered from the coal tar in the tar products plants. There are many uses for naphthalene. It is used as an insecticide against moths as moth-balls and naphthalene flakes and as a constituent in some candles. Its largest applications, however, are in the production of β -naphthol, chlorinated naphthalenes, and of around 180,000,000 pounds per year of phthalic anhydride, which is widely used in the manufacture of synthetic resins, plasticizers and in certain large groups of dyes. Considerable amounts of anthracene are recovered at some by-product coke and tar plants, and it has been extensively used in the manufacture of the poly-genetic dye, alizarine. The recent development of synthetic processes to manufacture anthraquinone from phthalic anhydride and benzene has reduced the markets for coal-tar anthracene. In recent years some phenanthrene has been recovered and used, and research is in progress to develop more uses for the higher aromatic hydrocarbons which could be obtained from coal tar.

Recovery of Aromatic Nitrogenous Bases

Several nitrogen-containing ring compounds are present in small quantities in the volatilized materials from coal carbonization. Among

these are pyridine, quinoline, isoquinoline, picoline and carbazole. Most of these substances are present in coal tar but up until about twenty years ago they received little attention. However, the increasing use of sulfa drugs and other synthetic medicinals, certain vitamins, rubber and other water-repellent materials has led to extended research in this field. Pyridine and other nitrogenous bases may be separated from the waste liquors after removal of the tar acids, by treatment with dilute sulfuric acid to form the corresponding sulfates and, after separation from the oil, by springing the sulfates with an alkali. For pyridine the chemical reactions might be as follows:



and



Pyridine is separated from the aqueous solution and may be purified by distillation. The production of crude pyridine increased from 86,532 gal in 1938 to 581,000 gal in 1945.⁶⁻²⁵ Continuous and batch processes for the recovery of pyridine are in operation. Present indications are that there may be further increases in the production of pyridine and some other nitrogenous bases. Thus, more of the former by-product coke plant wastes, through scientific and technological research, will be manufactured into useful products.

Phenols, Disposal and Recovery

Last but by no means least, from the standpoint of public interest, is the problem of removing the phenols from the effluents from the by-product coking and tar products plants and city gasworks. The phenolic substances present in the coal gas as it comes from the coke ovens are phenol, *o*-, *m*-, and *p*-cresols, xlenols and traces of higher homologs. A large proportion of these compounds, "tar acids," is in the coal tar. At the tar products plants, the tar is first distilled yielding several fractions of distillate and a residue of pitch. The tar acids are extracted from certain distillate fractions, chiefly from the lower-boiling oils. Although these tar acids are important products of the tar plants, they constitute only a few per cent of the total derivatives. Their chief uses are for manufacture of phenolic plastics and for preparation of disinfectants. From a tonnage standpoint, the major products of a tar plant are creosote oil and pitch. Creosote oil finds wide application as a wood preservative in the "creosoting" of railroad ties, harbor piling, wooden trestles and bridges, telephone poles, and fence posts. The production of coal tar in the United States in 1948 was 738,755,106 gallons and, in addition to the creosote oils, more than two hundred organic compounds have been iso-

lated from it. Some of these compounds, such as benzene, toluene, solvent naphthas, phenol and naphthalene are in part used directly, and in part as the starting materials along with other of the recovered compounds for the synthesis of thousands of useful substances, dyes, medicinals, explosives, perfumes and flavoring extracts. The remaining pitch is used as a construction material for roofs, roads, tar-paper siding and other purposes.

There are only relatively small amounts of phenol and the cresols in the aqueous ammonia liquors which are processed in the coke plants for by-product recoveries. However, through investigations made from around 1918 to 1929 by Baylis,²⁰ Ellms and Lawrence,⁶⁷ Hodge,^{101a} Howard,¹¹² Kohman,¹²¹ Streeter,²⁰⁴⁻⁶ Theriault,²¹¹ and others, it was discovered that even traces of phenol or chlorophenol present in water supplies imparted unpleasant tastes and odors. It has been stated that some persons can detect the taste of phenol in concentrations of only 0.1 ppm, and of certain chlorophenols as low as 3 ppb, but other persons may not notice the characteristic medicinal taste even in much stronger concentrations. The removal of the unpleasant tastes and odors is usually accomplished at city water-works by the application of activated carbon, such as "Nuchar" chlorine dioxide,^{7,21,218} break-point chlorination, or ozone. Some state water pollution control agencies have placed limits on phenol in parts per billion (ppb) when properly dispersed in the receiving waterway. The International Boundary Waters Commission of the United States and Canada has placed such a limit at not to exceed 5 ppb. The author's first experience with this problem was in 1921-24 when, by means of a stream survey of a section of the Monongahela River in West Virginia, and the cooperation of a tasting squad, the source of the unpleasant taste in the municipal water supplies of Morgantown, West Virginia, and South Pittsburgh, Pennsylvania, was traced by Hodge^{101a} to the effluent from a by-product coke plant which discharged its waste liquors into this river. The coke company installed, as soon as possible, a dephenolizer which recovered, according to Jones,¹¹⁴ around 96 per cent of the phenol from the plant effluent, and very seldom thereafter was there any medicinal taste in the Morgantown municipal water supplies. This was one of several investigations in progress in this country and in Europe during the years immediately following World War I. The conditions became so serious in the upper Ohio River Basin that the officials of the Health Departments of several of the states in that area organized the Ohio River Basin Interstate Stream Conservation Agreement (a forerunner of the present Ohio River Valley Water Sanitation Compact), and through cooperation with the U.S. Public Health Service, the by-product coking industry, and the iron and steel industry, installations of dephenolizers were made at nineteen plants to remove the

phenols from their respective plant waste liquors. The accomplishments of this cooperative effort have been well described by Waring,²²⁰ Stevenson,²⁰¹ Holmquist,¹¹¹ and Tisdale.²¹⁶ The operations of the dephe-nolizers greatly reduced the phenol being discharged to the streams, with resulting marked improvement in the quality of the water supplies drawn from the Ohio River and its tributaries.

Methods for Removal and Processes for Recovery of Phenol. In the first group of methods for removing the phenols from coke plant effluents no attempt is made to recover any of the phenols from the waste liquors. In this group there are the following methods:

(a) The ammonia still waste liquor is used in quenching the coke. This method is applied in some plants where the coke is used solely for charging into blast furnaces or foundry cupolas. The rate of corrosion of the iron and steel structures and equipment in the plant is greatly increased. According to Waring²²⁰ the corrosion increases from three to four times the usual rate. A quality of coke inferior for domestic uses is produced.

(b) Evaporation and then burning of the residue; accelerated corrosion usually results when this method is used. Rhodes¹⁷² reports that at one installation in Germany, all the waste water was evaporated directly into the air by gas-heated furnaces and most of the phenols were burned in the 250-foot high furnace stack.

(c) At one or two coke plants in this country, the phenols and ammonia in the waste liquors are vaporized to the atmosphere by a modified type of steam heating and distillation.¹⁴⁸ The process is said to require large amounts of steam. Since the ammonia liquors have not been treated with lime, there is little calcium chloride in the vaporized materials and the rate of corrosion in the plant is said not to be excessive, and atmospheric pollution has not been a serious problem.

(d) The frothing properties of the liquid wastes have favored their use at some coal flotation plants in Lower Silesia.¹⁷²

Biological Treatment of Waste Liquors from Coal Carbonization Processes. The earliest research on the treatment of waste liquors from gasworks and by-product coke plants was probably carried out in England. Prior to 1899, experiments conducted at the Manchester Gas Works showed that the thiocyanates and phenols in the ammonia recovery liquors could be largely destroyed when mixed to the extent of about 0.5 per cent with municipal sewage and subjecting the mixture to biological action.

An accidental discharge on December 2, 1899, of an abnormally large volume of gasworks waste liquor which contained a fairly large proportion of thiocyanates into the sewer occasioned some concern until it

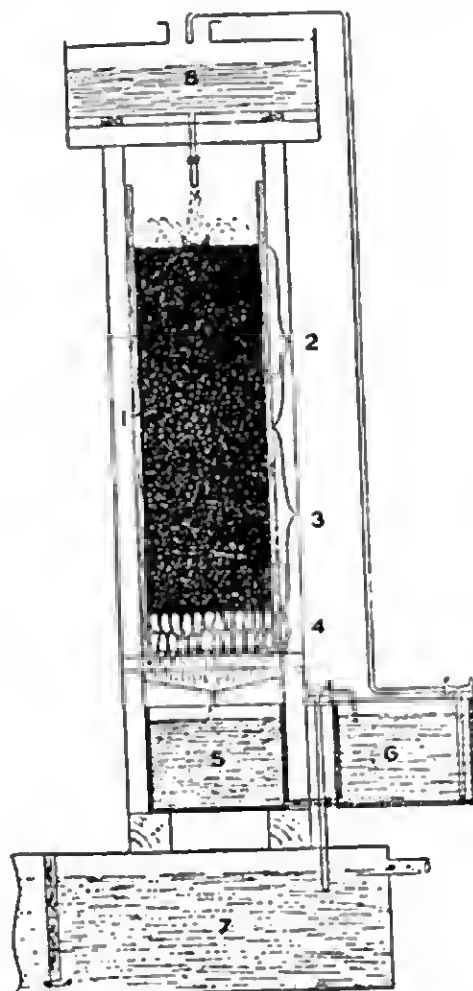
was found that the sand filters through which the contaminated sewage was percolating reduced the oxygen absorption from permanganate from 34.3 to 3.6 parts per 100,000. Shortly thereafter research was undertaken by Frankland and Silvester⁷⁷ on the biological treatment of gasworks effluents. Extensive investigations were made on the sewage of Oldbury, England, which at dry weather flow amounted to 791,000 gal/day and contained approximately 9 per cent of waste from the distillation of ammonia gas liquor. Experiments were conducted on double and triple sets of bacterial contact beds and on a similar number of trickling filters. They concluded that as much as 9 per cent of the ammonia recovery liquor from the gasworks when mixed with city sewage could be satisfactorily purified on triple bacterial contact beds, and fairly satisfactorily by the set of trickling filters.

About this same time Fowler, Arden, and Lockett⁷³ began an extensive investigation on the bacterial purification of ammonia recovery liquor. The investigations were carried out on a laboratory scale using bacterial filter beds, and involved the aeration of solutions of phenols and thiocyanates diluted with sewage. They found that oxidation to ammonia, nitrate, and sulfate was fairly complete. They isolated from the mixture a microorganism, probably *B. helvolus*, which utilized phenol, but considered that the oxidation of the thiocyanates was caused by the combined action of several types of microorganisms. A solution of phenol which contained about 100 ppm was reduced to 2 ppm by aeration for 19 days but only after the phenol solution had been inoculated with sewage. Experiments with bacterial filters showed that sewage containing up to 187 ppm of thiocyanate and up to 680 ppm of phenols was readily oxidized. The results on the laboratory experiments conducted by Fowler and Holton⁷⁴ were sufficiently satisfactory so that the investigation was continued using a small bacterial filter containing 4 cubic yards of crushed clinker for the purification of ammonia recovery liquor (Figure 24). Ten per cent of the waste liquor was diluted with effluent from the filter bed and then passed through the bed of clinker supporting the microorganisms which effected purification of the waste liquor. Approximately 100 gal/day/cu yd was determined as the optimum rate of flow. A purification of approximately 90 per cent, calculated on the crude liquor, resulted by this treatment. This bacterial filter was operated for 6½ years with satisfactory results.

Investigations along this line were also carried on by Fowler and Shepherd⁷⁵ at the chemical works of the Bradford Corporation on a larger scale than had been previously attempted. Some difficulties were encountered but were overcome and successful treatment of the ammonia recovery liquors was obtained by the bacterial filter bed handling up

to 3,500 gallons of waste liquor per 24 hours. The total purification attained was estimated as over 98 per cent. Phenol-utilizing micro-organisms were isolated from the filter effluent.

Researches on the biological treatment of ammonia still wastes and phenols have been continuously carried on since those early reports.



(Courtesy, *J. Soc. Chem. Ind.*, 30, 181, 1911)

FIGURE 24. An early type of experimental bacterial filter for treating ammonia still wastes

Much of the information on these succeeding investigations is contained in the Transactions of the Institution of Gas Engineers, and has been summarized up to 1938 by Key.⁶⁻⁹ In discussion of the over-all results Key concludes that if ammonia still waste does not constitute more than 0.5 per cent of the volume of ordinary sewage in the activated sludge sewage disposal process, the effect on the operation of the process will not be serious. However, the effects do vary with the type of sewage load, and the quantity of ammonia waste liquor which can be tolerated by

a given sewage treatment plant has to be determined for that plant. He states that difficulty in oxidation of gas waste products is in the order of phenols, higher tar acids, thiosulfates and thiocyanates.

Writing in 1932, Slater¹⁸⁹ states that 0.5 per cent of gas liquor in the city sewage at one city treatment plant was seriously interfering with the purification of the sewage. However, by giving the sewage and gas liquor mixture a preliminary filtration treatment through a sand filter, the 4-hour oxygen absorption was lowered from 126 to 38 ppm.

The toxicity of the constituents in gasworks waste liquors has been investigated by many workers. Southgate, Pentelow and Bessindale¹⁹¹ investigated the causes of the killing of salmon and sea trout smolts in the estuary of the River Tees and concluded that the tar acids and cyanides from the coke plant effluent were the cause. Southgate^{191,192} made further studies of the toxicity of coke oven effluent discharged into the estuary of the River Tees. He concluded that the main toxic substances present in the waste liquor were the tar acids and the cyanides, the latter being the more toxic. He found that the cyanides could be converted to the harmless ferrocyanides by agitation with ferric chloride. Any hydrogen sulfide present interfered with the reaction on cyanides by forming iron sulfide. If the mixture was aerated, an increased rate of reaction of the cyanides was obtained. Another method applied was spraying liquor at 58°C through the air as a fine mist. By this method the toxicity of the cyanides was reduced to about one-sixteenth of its former value. These investigations and many others are well summarized by Southgate^{6,19} in a book published in 1948, and in a paper published in 1949.¹⁹³

Experiments on the biochemical decomposition of phenol in natural water led Bach^{12,14} to conclude that phenol in amounts up to 25 ppm was readily destroyed within 4 or 5 days. Concentrations of phenol in an amount up to 10 ppm appeared to have no harmful effect on goldfish. However, after the goldfish had lived in water containing 15 ppm phenol for 46 days, the flesh of the fish had a faint odor of phenol. In investigations on the tastes caused by phenol in water, Bach found that one part of phenol diluted in 125,000,000 parts of Essen City water after chlorination produced a noticeable and unpleasant taste.

In further researches on the Emscher tank, Bach^{10,11,13,15,17,18} found that gas production was practically completed in 60 days and that the ratio of organic matter in raw sludge compared to that in the digested sludge from four different tanks was 1.25, 2.0, 1.24 and 1.54. The composition of the gas was generally of the order of approximately 20 per cent CO₂, 70 per cent CH₄ and 10 per cent N₂ and H₂. He discussed the relative advantages of the Emscher contact bed and

trickling filters and concluded that for treatment of certain industrial wastes, particularly phenolic wastes, and those from certain food and dairy industries, the Emscher contact bed has special advantages.

A study of the different kinds of soil bacteria which decompose certain organic compounds was made by Gray and Thornton⁸¹ who found there were several types of bacteria which would decompose phenol, ortho-, meta- and para-cresols, phloroglucinol and resorcinol. Such bacteria were found to be widely distributed in Great Britain and have been found in soil from Norway, the Tyrol and the South Atlantic Islands. They rarely occur in unfertilized soil. The organisms of this type fall into seven genera and twenty-five species. When soil is treated with phenol an increased bacterial population ensues, composed largely of *micrococcus spheroides* n. sp., which decompose phenol in pure culture. Certain strains of soil bacteria which utilize several phenolic compounds have also been isolated by Bartels.^{19a}

Two other biological processes for the treatment of phenolic waste liquors described by Nolte¹⁵⁶ have been developed in Germany. One is known as the phosphate "P-process"; the other known as the Schönbürg ("Tri-process") which is especially applicable to the highly concentrated wastes. It has been suggested that the "P-process" might be used for the dilute phenolic waste liquors and to supplement the "Tri-process" which had been used to treat the concentrated wastes.

Nolte, Meyer and Fromke¹⁵⁹ have patented a biological treatment process for the decomposition of phenols in which the phosphates are added to the waste waters. The process appears to resemble the activated sludge process supplemented by additions of available phosphates. Calculations for the construction and operation of the Magdeburg "P-process" for the treatment of phenol-containing sewage have been given by Nolte.¹⁵⁷

Nolte and Boudt¹⁵⁸ conducted experiments on the biological sewage treatment with activated sludge in the presence of cyanogen in connection with the waste waters from the low temperature carbonization of coal. The waters were high in phenols and cyanogen. Results of the investigations indicated that the decomposition of the cyanides and phenols was purely bacteriological rather than through the combined action of bacteria, protozoa and other microorganisms, as previously thought. The difficulties in the biological treatment of the cyanide-containing wastes were attributed largely to the toxicity of the metals associated with the cyanides.

A number of investigations have been conducted in the United States on the use of biological processes for the satisfactory treatment of ammonia still wastes and phenol-containing waste liquors. One of the

early investigations along this line was sponsored by the Koppers Company, Inc., at its Seaboard by-product coke-oven plant. Treatment of the phenol-contaminated liquors was studied first in the laboratory and then on a pilot-plant scale. It was found that by properly diluting the liquor and controlling the rate of flow through a filter containing humus material which held the phenol-destroying microorganisms that the phenol content of the waste liquor was greatly reduced. A patent on this process was granted to Brown²⁹ in 1922.

The pioneer investigations in the United States on the treatment of ammonia still wastes by the activated sludge process were carried on by the Milwaukee, Wisconsin, Sewerage Commission.¹⁴³ The wastes from the coke plant were being discharged into Lake Michigan, from which Milwaukee obtains its municipal water supply, and at times the water had an objectionable taste. Experiments were undertaken to see if the still waste could be treated in the municipal sewage treatment plant. The results of the extended investigation showed that when the still wastes were diluted in the sewage so that the resulting mixture contained only about 2 per cent of ammonia still waste, the effluent from the treatment plant was free from phenol as determined by taste tests. Further experiments showed that the content of the phenolic wastes could be satisfactorily treated at considerably higher than the 2 per cent concentration. In some cases mixtures containing as high as 15 per cent were satisfactorily treated. The Milwaukee sewage entering the activated sludge plants contains about 18 ppm of phenol. Some English work has indicated that as high as 150 ppm phenol can be destroyed when properly mixed with domestic sewage. The quantity of the still wastes which can be satisfactorily destroyed by the activated sludge process depends considerably on the temperature and quality of the sewage. A considerably higher content of phenols in the sewage can be satisfactorily destroyed during warm weather conditions but in cold weather the quantities of phenolic substances should be proportionately lower if satisfactory results are to be obtained.

An important contribution to this subject was made by Mohlman^{144,145} who conducted extensive laboratory experiments on the quantities of still waste which could be mixed with municipal sewage and still obtain satisfactory reductions of the phenols and the 5-day biochemical oxygen demands (BOD) of the mixtures. The results of the laboratory experiments showed that additions of less than 2 per cent considerably increased the 5-day BOD values. The organic nitrogen and total bacteria were also increased perceptibly. Experiments were then carried out in the large activated sludge sewage treatment plants of the Chicago Sanitary District. It was found that this process could

handle sewage well mixed with ammonia still wastes when the mixture contained as much as 30 to 40 ppm of phenol without serious impairment of the quality of the effluent. Mohlman also observed that the phenols oxidized much more readily at the higher temperatures. At a temperature of 20°C the phenol content decreased to 100 ppb in 3.4 days, while at 10°C it required 7.4 days for a similar decrease in phenol content. Discussion of Mohlman's paper by W. A. Ryan emphasized the fact that the oxidation of phenolic wastes is not a purely chemical oxidation but requires the assistance of certain types of aerobic bacteria. A summary of the results obtained by Mohlman is given in Table 14.

Several other investigations along these lines have been carried out, a recent one being that by Mathews¹⁴¹ on the treatment of ammonia still wastes by the activated sludge process in Gary, Indiana. This was a cooperative investigation sponsored by the officials of the Gary Sewerage Commission and of the United States Steel Company. The investigation was started on October 27, 1950, and extended until April 30, 1951. The ammonia still wastes were carefully freed from suspended solids, tars and oils and were fed into the municipal sewage at a carefully controlled rate. The maximum load anticipated was from 1,500 to 2,000 pounds of phenol per day in 500,000 gallons of ammonia still waste liquor. The flow of sewage to the plant was around 20,000,000 gallons per day. Certain changes were made in the plant operation. More aeration was, naturally, required to handle the additional load, and certain other factors had to be adjusted. However, the phenols were destroyed to an average of 99.94 per cent and the effluent from the sewage treatment plant contained only a few ppb of phenols.

Shnideman and Bowman^{184a} investigated the action of anaerobic organisms on phenolic wastes. The ammonia still waste was added to the sewage in the ratio of 1 part to 2,000 parts and subjected to sludge digestion in Imhoff tanks. No ill effects were observed in the operation of the Imhoff tanks. Only a small proportion of the phenol was destroyed by this method and they suggest that the trickling filter or the activated sludge processes would probably give better results in the destruction of phenols.

In discussion of biological treatment of soluble organic wastes, Rudolfs¹⁷⁵ states that the BOD values of soluble organic wastes vary from 1,000 to 50,000 ppm. Treatment by physical or thermal means such as evaporation or distillation is usually not feasible and treatment with chemicals is often expensive and may produce large volumes of sludge which are difficult to handle or may in other ways change one waste disposal problem into another of equal or greater magnitude. He considers that treatment by biological means, aerobic or anaerobic,

is often the most practical method for treating some industrial wastes. The degree of purification naturally depends upon the biological process applied and, in general, Rudolfs considers high rate filters are preferable to the activated sludge process. Some of the industrial wastes require the addition of available nitrogen and phosphates to maintain the maximum number of microorganisms for efficient decomposition of the liquid wastes. Purification up to 95 per cent or higher is often possible.

The practical application of the biological processes for the destruction of organic wastes, including phenols, is well illustrated by the large waste treatment plant of the Dow Chemical Company at Midland, Michigan. Descriptions of this plant and its operation have been given by Harlow, Powers, and Ehlers,⁸⁷ and by Harlow and Powers.⁸⁸ At this plant the mixture of liquid wastes from the manufacture of many organic compounds is discharged to a 45,000,000-gallon settling and equalizing pond in which the suspended solids settle and the different wastes become well mixed. The effluent from this pond is neutralized with lime and then flows to a clarifier; the clarified overflow goes to trickling filters in which a considerable reduction of BOD and phenol content takes place. The effluent from the filters flows to a second settling pond, then to the activated sludge plant in which further reduction of the BOD and phenol content of the waste water is accomplished, and the effluent goes to a third settling pond for a suitable detention period. The oxidation capacity of the activated sludge plant is about 1,700 lb per day of phenol, or 5,000 lb per day of BOD. The soluble organic substances are further oxidized in the effluent ponds and the biological flocs and other suspended materials settle before the purified waste waters are discharged to the river. By these processes the phenol contents of the plant's waste liquors are reduced sufficiently to meet the requirements of the International Boundary Commission of the United States and Canada which specify that there shall be not over 5 ppb of phenol in the receiving waterway after a plant's effluent is well dispersed therein.

Bacteriological Studies of Phenol-Destroying Microorganisms. Investigations as to the species of bacteria or other microorganisms which attack phenolic compounds have been undertaken in recent years. The activity of *Achromobacter* in the destruction of mono-, di- and trihydroxy phenols was investigated by Skarzynski and Czekalowski.¹⁸⁸ They found that species of these bacteria would attack nearly all of these compounds. The presence of a free phenolic group in the compound was essential for bacterial action.

The effects of bacterial actions on phenol or the presence of other organic solvents in the waste waters was investigated by Cooper.⁴⁵ He found that ethylene glycol, monobutylether and propylene oxide

were germicidal against *Bacillus lactis aerogenes* in a 10 per cent concentration solution and against *Staphylococcus* at 3 per cent concentrations. The addition of acetone to a test solution increased the bacterial action on phenol and benzyl alcohol more than it did on solutions of *p*-cresol, thymol and chlorophenols. The effects of other organic compounds on the activity of bacteria in destroying phenols were also investigated and results indicated a certain degree of selectivity in the activity of the bacteria.

The effect of soil microorganisms on a number of aliphatic and aromatic oxygen-containing compounds, including phenolies, was investigated by Kameda and Toyoura.¹¹⁵ They found a number of strains of soil bacteria which would attack many of the compounds investigated. However, certain strains of bacteria would attack some compounds and not attack others of a nearly similar chemical structure. This, also, shows the specific action of microorganisms.

The oxidation of phenol and benzoic acid by some soil bacteria has been studied by Evans.⁷¹ The experiments were carried out in a simple mineral salts medium inoculated with bacteria from soil, sewage and fecal matter. The phenol and benzoic acid or their derivatives were present as the sole sources of carbon. A number of the compounds were destroyed by the biological activity, and analyses of products formed led to the conclusion that the oxidation of the side chains is followed by a splitting of the nuclear ring and its subsequent oxidation.

The utilization of microorganisms for the disposal of industrial wastes has been investigated and discussed by Buswell.³² He concluded that there is a large field for investigations on the applications of bacteriology in the treatment of sewage and trade waste waters, and for the development of uses for the products from the treatment of sewage and of certain industrial wastes.

The effects of phenol, chlorophenols, and cresols on natural waters have been investigated by Streeter²⁰⁴ and others of the U.S. Public Health Service. One of the latest contributions along this line is that by Ettinger and Ruchhoft.⁶⁹ In their studies the samples of river water were analyzed after appropriate amounts of 1,000 ppm of phenolic materials had been added and the samples stored for varying periods of time. The rate of dissimilation of phenols was found to depend upon the following factors: metabolism controls of microbiological agencies, temperature, microbiological lag, microfauna and flora present, the specific compounds and amounts involved, and the presence of auxiliary nutrients such as available nitrogen and phosphorus which made possible the metabolism of the phenolic materials. The general conclusion from a series of laboratory researches and investigations made on the

Ohio River and other streams by the U.S. Public Health Service is that the removal of the phenolic substances in natural waters cannot be accounted for by atmospheric oxidation or chemical means alone, but requires the action of phenol-utilizing microorganisms. The action of *Pseudomonas fluorescens* grown on mandelate, benzoate, or phenol showed complete adaptation to catechol but not to protocatechuic acid, investigated by Sleeper and Stanier.¹⁹⁰ Cells were also grown on some other aromatic compounds of large structure, but other compounds gave negative results.

The Warburg respirometer was utilized by Stanier, Sleeper, Tsuchida, and MacDonald¹⁹⁸ to investigate the bacterial oxidation of aromatic compounds. They applied enzymes from *Pseudomonas fluorescens* to catechol, protocatechuic acid and other aromatic compounds, including phenol, and found the substances were oxidized to β -ketoadipic acid and not to carbon dioxide as is the usual case when using living cells.

Kramer and Doetsch^{123a} studied the growth of phenol-utilizing bacteria on aromatic compounds. They used the media described by Gray and Thornton⁸¹ with 55 different aromatic compounds in concentrations of 0.01, 0.001 and 0.005M as a source of carbon. They isolated fourteen phenol-utilizing organisms of the genera *Achromobacter*, *Vibrio* and *Micrococcus* from the soil and tested for growth on the media. The results of the tests with different strains of bacteria indicated that many of the aromatic compounds were attacked by certain strains of bacteria.

Investigations as to the presence of phenol-utilizing microorganisms in the rivers in the vicinity of Pittsburgh, Pennsylvania, were conducted by Hodge and Tallon.¹⁰⁷ Mineral salts media were used in the investigations and phenol-utilizing microorganisms were found in many of the streams and in certain industrial wastes being discharged to the streams. The results are shown in Table 19. Some of the strains of bacteria isolated from the cultures developed in the river waters were transferred to suitable media and then subjected to tests as to the concentration of phenol which they could tolerate. Some of the strains of bacteria perished in concentrations of phenol in mineral salts media containing only about 300 ppm of phenol. By successive inoculations, other strains were developed until they showed vigorous viability in mineral salts media containing as much as 1,000 ppm of phenol as the only source of carbon. When cultures of the highly resistant-to-phenol strains of bacteria were inoculated into some industrial wastes and the mixtures aerated, the reduction of their phenol contents was accelerated. In other experiments the bacteria apparently perished, probably due to some toxic substance in the waste liquor, and on aeration only small reductions were obtained of the phenol content of the industrial waste. The

TABLE 19. ISOLATION AND DEVELOPMENT OF PHENOL-UTILIZING MICROORGANISMS¹⁰⁷

Source of the Microorganisms	Phenol Tolerance in Mineral Salts Media (ppm)	
	Phenol Concn. of Media in which Organism was Isolated	Tolerance Developed to Phenol Concn. of
A. Industrial Waste Liquors		
Iron and steel plant effluent, sample 1	400	...
Iron and steel plant effluent, sample 2	400	...
Iron and steel plant effluent, sample 3	400	...
Iron and steel plant effluent, sample 4	400	1,000
Tar products plant effluent	400	700
Wood preserving plant effluent, sample 1	400	1,000
Wood preserving plant effluent, sample 2	400	500
B. Rivers and Creek		
Ohio River, Pittsburgh, Pa., sample 1	400	...
Ohio River, Pittsburgh, Pa., sample 2	400	...
Ohio River, Sewickley, Pa.	400	...
Ohio River, Ambridge, Pa.	400	1,000
Ohio River, Rochester, Pa.	400	1,000
Ohio River, Montgomery Dam, Pa.	400	1,000
Ohio River, Shippingport Ferry, Pa.	400	...
Beaver River, Beaver, Pa.	400	1,000
Monongahela River, Pittsburgh, Pa.	400	1,000
Youghiogheny River, McKeesport, Pa.	400	...
Bear Creek, Petrolia, Pa., sample 1	400	...
Bear Creek, Petrolia, Pa., sample 2	400	...
Bear Creek, Petrolia, Pa., sample 3	400	...
C. Municipal Sewages		
Municipal sewage, sample 1	400	...
Municipal sewage, sample 2	400	...
Municipal sewage, sample 3	400	...

Hodge, W. W., and Tallon, G. R., Koppers Company's Effluents Treatments Fellowship, Mellon Institute.

possibility of developing strains of microorganisms which will destroy phenolic compounds in high concentration waste liquors may be worthy of further investigation. The use of bacteria and other microorganisms for the treatment of industrial wastes and for the production of useful materials appears to be a very active field of research at the present time.

Another recent contribution to the biological method of treating ammonia still wastes was made by Nicklin¹⁵⁵ in 1948. He describes the method of treating the waste liquor from a gasworks which is making 14,000,000 cubic feet of gas per day and carbonizing the coal in intermittent vertical chambers. The method of treating the gasworks liquor is similar to that adopted by the City of Coventry Corporations Gas

Department. Four bacterial beds on which the waste liquor is purified are each 120 feet in diameter and are filled with $4\frac{1}{2}$ to $5\frac{1}{2}$ feet of graded granite as follows: 6 inches of 6-inch granite, 1 foot of $1\frac{1}{2}$ -inch, 1 foot of 1-inch, and $2\frac{1}{2}$ feet of $\frac{3}{4}$ -inch granite. The area occupied by the beds is one acre. The total volume of filtering material is 7,700 cubic yards and the distributors are standard 4-arm sprinklers. For the treatment of 32,400 gallons per day a total of 6,140 cubic yards of filtering material is required; this figure represented the four filter beds after allowance had been made for overload. The beds were first matured with domestic sewage diluted with brook water and purified effluent. Some humus from the sewage works was also added to the bed. The dosing rate was gradually increased to 122 gallons per cubic yard of filtering material per day. The mixed liquor fed to the filter beds was composed of one part ammonia spent liquor diluted with 23 parts purified effluent (i.e., recirculation 23 times the volume of spent liquor). The oxygen absorption value of the spent liquor was 890 pp 100,000 and that of the effluent discharged to the sewers was 62 pp 100,000. This indicated a purification efficiency of around 93 per cent. After working for 12 weeks the beds were rested and then used for treating 3,170,000 gallons of spent liquor. The filters gave the following results: The oxygen absorption value of the spent liquor was 1050 pp 100,000 and of the effluent 145 pp 100,000, which indicated a purification efficiency of about 86 per cent. The second period of operation was carried out under cold weather conditions, at times, with ice on the filter beds. However, the general conclusions are that this bacterial method of purification requires a large ground space and is rather expensive for treating crude waste liquors. It might be applicable as a final purification process after the larger portion of the phenols had been removed by mechanical or thermal methods.

A process for destroying the phenols in railroad car washings has been developed by the General American Transportation Corporation and is in operation at one or more car cleaning yards in the United States. In this process, as installed in the Corporation's treatment plant in Saegerstown, Pennsylvania, and described by Gutzeit^{84,85,86} the wash waters, after removal of settleable solids and oily contents, are thoroughly mixed with finely ground bituminous coal, which adsorbs nearly all the phenol in the liquid wastes. Most of the coal with its adsorbed phenol is separated from the waste waters by application of froth flotation cells and rotary, drum filters. The coal filter cake may be burned, thus destroying the phenols, or it may be hauled to a suitably located dump. The filter effluent contains a small amount of phenol and some very finely divided coal. The coal is settled out in a clarifier, and

the clear overflow liquid goes to a trickling filter (Figure 25). During warm weather the remaining phenol is destroyed by the biological activity in the trickling filter, but during the cold months, the effluent from the trickling filter is given sufficient applications of chlorine dioxide to complete the destruction of phenols. This process is reported to reduce the phenol contents of the final effluent to a few parts per billion and to have received the approval of certain state water pollution control authorities.



(Courtesy, General American Transportation Corporation)

FIGURE 25. Trickling filter used for final destruction of phenols in waste liquors. The clarifier is in the foreground and the settling pond to the rear of the filter

The application of chlorine has proved successful in destroying the phenols in the effluent from the rubber reclaiming plant of the Pequannoc Rubber Company, Butler, New Jersey. The extensive laboratory research and pilot-plant investigations conducted to develop processes for satisfactorily treating the acidic and alkaline waste liquors, and the design of the industrial size treatment plant have been described by Secrist and Chamberlin,¹⁷⁸ and by Chamberlin and Griffin.³⁸ Suspended solids are removed in primary and secondary settling basins; applications of copperas and lime to the alkaline wastes completed their clarification and removed much of the color and odor. The treatment with chlorine completely destroys the phenols in the waste liquor and removes nearly all the remaining color and odor before or during the retention time in a final storage basin. In the treatment plant under construction the clarified and properly treated originally acid and alkaline waste liquids are combined and will pass through upflow limestone filters before discharge to the river. Careful pH controls for optimum operating conditions are maintained in all sections of the treatment plant.

Dephenolization Processes for Recovery of Phenol. During the past thirty years a number of processes have been proposed for recovering

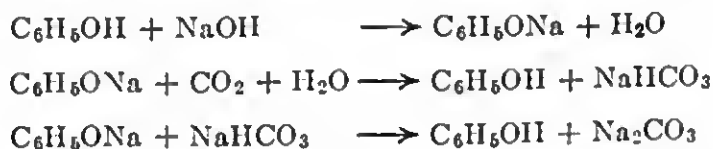
the phenols from the waste liquors from by-product coke and tar processing plants and gasworks, and a few have been developed to commercial operations. The processes may be classified into three general types, as follows:

- (1) Absorption, countercurrent liquid extraction.
- (2) Adsorption on solid media.
- (3) Vapor-phase dephenolization.

Under type (1), at least five processes have been developed to industrial installations. Based on the composition of the extraction solvent applied and the types of equipment used, they are:

- (a) Benzene or light oil process.
- (b) Triresyl phosphate, or "Triphos" process.
- (c) Phenosolvan process.
- (d) Holley-Mott process.
- (e) Lowenstein-Lom process.

(1) Absorption, countercurrent liquid extraction. This type of process is based on the absorption of the phenol in the waste liquor by having it come into intimate contact with a counter-flowing extraction solvent which has a favorable distribution coefficient for phenol compared to that of water, and which is only sparingly soluble in water. The phenol-containing solvent is treated with an alkali, usually sodium hydroxide, which reacts with the phenol to form sodium phenolate which is nearly insoluble in the extraction solvent and separates from it. Most of the solvent is recovered, and reused. The phenol is removed from the phenolate by springing it with an acid. Sulfuric acid was generally used, but for some years past flue or stack gases high in content of carbon dioxide have commonly been applied. The general chemical reactions for phenol recovery might be shown as follows:



If sulfuric acid is used, then sodium sulfate instead of sodium carbonate is formed. The sulfate must be disposed of and the cost of the sulfuric acid is charged against the process.

Benzene or Light Oil Process. The solvent used in the first dephenolizers of this type was benzene, but later some companies used certain portions of the light oils.⁴⁸⁻⁵⁰ The benzene countercurrent dephenolizer was the first type developed for industrial installation and there are several of

these dephenolizers in operation in Europe and the United States. A dephenolizer of this type constructed at a by-product coke plant in 1926-27 was stated by H. E. Jones¹¹⁴ at that time to recover 96 per cent of the phenol from the coke plant's liquid wastes, and Knight¹²⁰ reported that in 1951, this dephenolizer was still removing from 94 to 96 per cent of the phenol in the waste liquors. The Enscher-genossenschaft, which originally used this process, has, according to Rhodes,^{171,172} changed to the Pott-Hilgenstock modification for continuous extraction of phenol from the benzene by caustic soda solution. A general flow diagram of the benzene countercurrent type of dephenolization process is shown in Figure 26.

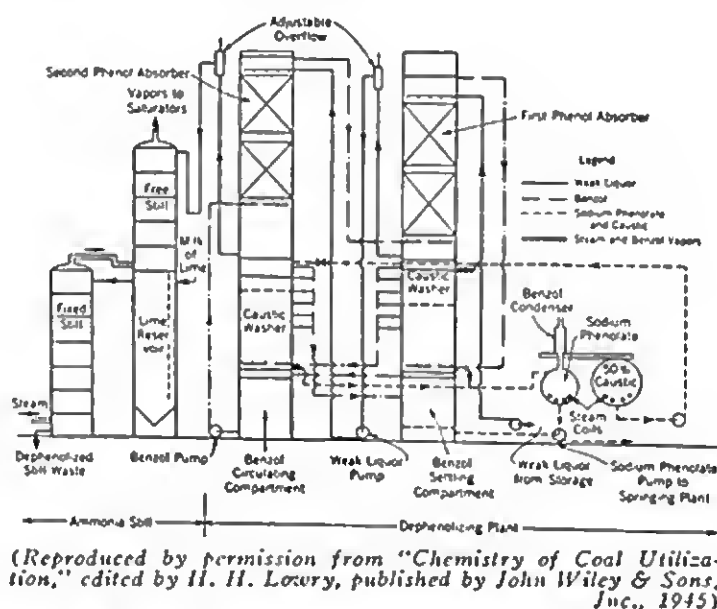


FIGURE 26. Flow diagram of a solvent-dephenolization process

The Tricresyl Phosphate Process. This process was developed by the I. G. Farbenindustrie in Germany and used tricresyl phosphate as the extraction solvent, which has a very favorable partition coefficient for phenol in aqueous solutions, as shown by Tupholme.²²³ An installation of this process made in Germany has been described by Rhodes.¹⁷¹ Difficulties in operation, especially the recovery and purification of the expensive solvent, prevented the general adoption of this process by the by-coking industry. Extensive investigations were conducted by the Koppers Company, Inc., on the applicability of this process to American coke-oven practice, but the results were not encouraging and there are no installations of the "Triphos" process in the United States.

The Phenosolvan Process. In this process a mixture of comparatively low-boiling esters of the aliphatic series, principally isobutyl acetate, is applied to extract the phenols from the ammonia still and other waste

liquors. This process was developed in Germany by the Metallgesellschaft A. G., and in 1940, Lurgi and I. G. Farbenindustrie A. G. cooperated on the industrial promotion of this process, which is covered by several patents. The process has been described by Dierichs⁵⁹⁻⁶¹ in connection with the operation of a plant treating 30 eu m of aqueous liquor containing 4 g/l of phenol, which was reduced to 0.06 g/l, with a phenosolvan loss of about 200 g/eu m of water. The process is said to be satisfactory not only for extracting the monohydric phenols from the liquid wastes but also especially efficient in recovering the dihydric phenols, such as catechol, which occur in appreciable quantities in the volatilized materials from (1) the low-temperature carbonization of bituminous coal; (2) from the coking of central European lignite coals;

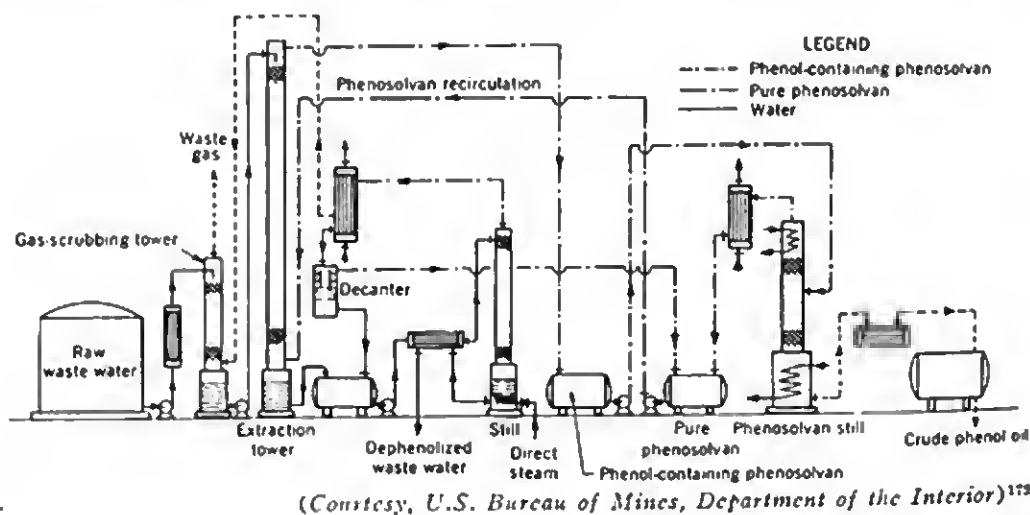
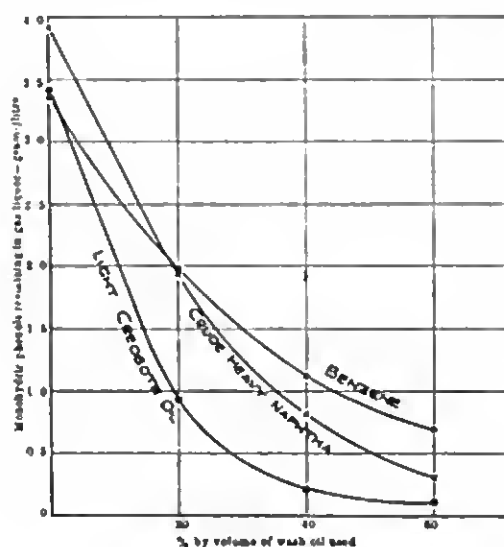


FIGURE 27. Flow diagram for dephenolizing low-temperature carbonization waste waters by the Phenosolvan Process, Lurgi

and (3) from certain types of coal hydrogenation operations.¹³⁶ Lowenstein-Lom, Schnabel, and Kejla¹³⁵ have reported the results of extensive research on the partition coefficients for phenols of a large number of aliphatic esters, ketones, secondary alcohols and ethers. They also discussed the other factors to be considered in the selection of the best solvent for the extraction of mono- and dihydric phenols from the waste liquors from high- and low-temperature coal carbonization plants. Investigations on the use of *n*- and isobutyl acetates and certain other compounds carried on by the Koppers Company's Fellowship in Mellon Institute and by other researchers in the United States have given satisfactory results in the extraction of phenols from the waste liquors of some American coking and chemical industries. There are no installations of the Phenosolvan process in America, but there are several in Germany; a flow diagram for one such plant described by Rhodes¹⁷² is given in Figure 27.

The Holley-Mott Process. This process has been in operation for several years at the Beekton Works of The Gas Light and Coke Company, London, England. The dephenolization plant was constructed to recover phenol from the ammonia liquor effluent amounting to about 80,000,000 gallons per annum. Phenol recovery ranges from 90 to 93 per cent, according to Murdoch and Cuckney.¹⁵⁰ The process is a modification of the procedures developed in 1925 by Thornton,²¹³ an engineer-chemist employed by the Anglo-Persian Oil Company in its operations in Asia Minor. It is a countercurrent liquid-liquid absorption process, but in place of the extraction towers or columns of different kinds, and vertical



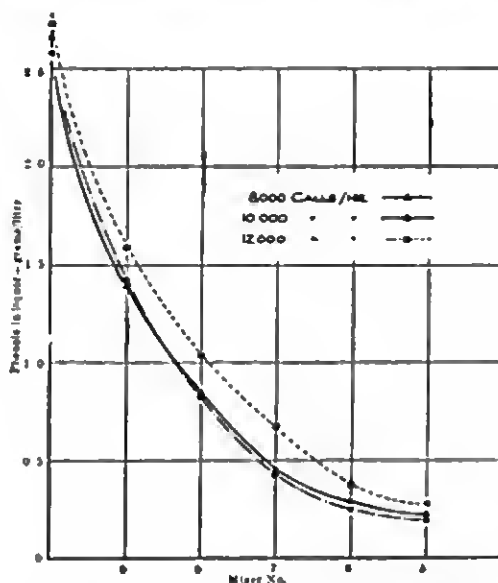
(Courtesy, Trans. Inst. Chem. Engrs.)

FIGURE 28. Removal of monohydric phenols from gas liquor by various solvents, using 3 washes of 20% by volume

countercurrent flow used in the three previously mentioned processes of type (1), in the Holley-Mott process a series of pairs of rectangular tanks are installed all at the same level. The tanks are so connected with pipes that by alternate mechanical mixing and gravity separation of the waste liquor and extraction solvent in a horizontally flowing, countercurrent, liquid-liquid system the phenols in the waste liquors are recovered in the solvent. Different solvents and mixtures of solvents have been successfully applied with somewhat varying efficiencies of phenol extraction. The removal of monohydric phenols by different solvents are shown in Figure 28, and the removals at successive stages of operation in Figure 29. The flow diagram of the Holley-Mott dephenolizer installation is shown in Figure 30

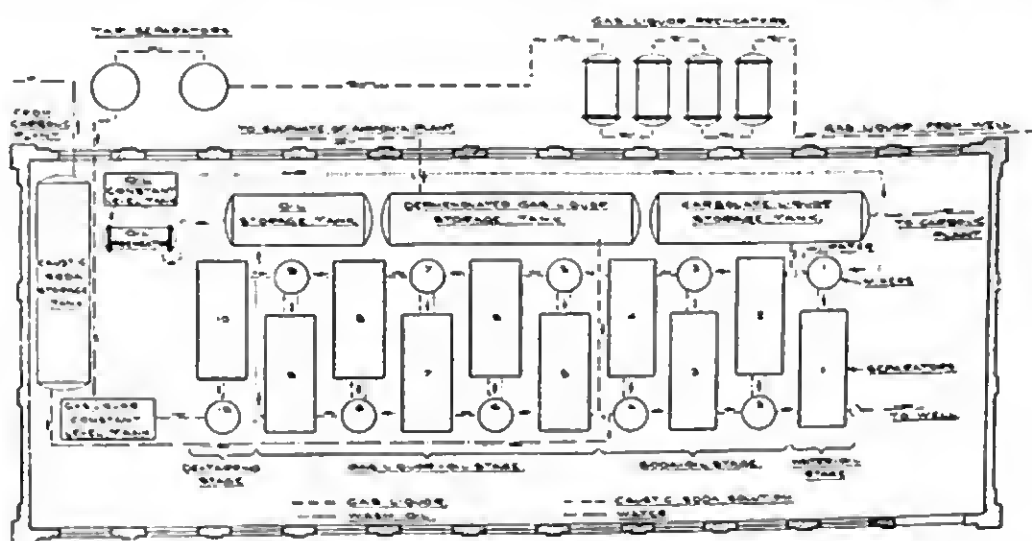
The Lowenstein-Lom Process. A recently developed liquid-liquid absorption process for the extraction of phenols from the liquid wastes

from the carbonization of coals, especially from the low-temperature coking of European lignites. Figure 31 shows a flow sheet for this dephenolization process.¹³⁶ In both the Holley-Mott and the Lowenstein-Lom processes advantage is taken of the favorable effects of additions



(Courtesy, Trans. Inst. Chem. Engrs.)

FIGURE 29. Removal of monohydric phenols at each stage in Holley-Mott plant



Diagrammatical layout of gas liquor dephenolization plant

(Courtesy, Trans. Inst. Chem. Engrs.)

FIGURE 30. Diagrammatical layout of gas liquor dephenolization plant, Holley-Mott process

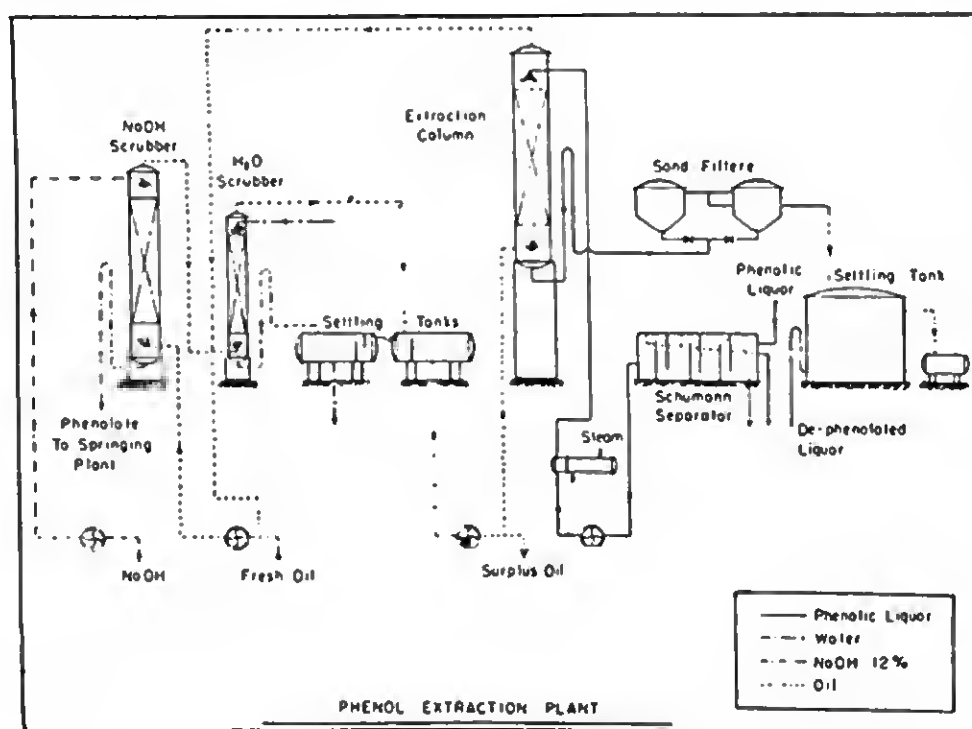
of aromatic nitrogenous bases, such as quinoline and isoquinoline, on the distribution coefficient of the main extraction solvent for phenol, as shown in Table 20. In the Lowenstein-Lom process when straw-oil

TABLE 20. THE EFFECT OF TAR BASES ON THE PARTITION FACTOR OF WASH OIL FOR MONOHYDRIC PHENOLS^{150,151}

% by Wt. of Base added to Wash Oil	Partition Factor Oil/Gas Liquor					
	0	1	2	3	4	5
Pyridine	1.8	4.6	7.7	9.9	11.9	14.6
Quinoline	1.8	...	7.1	10.5	12.7	15.8
Isoquinoline	1.8	15.8
Aniline	1.7	...	2.3	...	2.7	3.2

Murdoch, D. G., and Cuckney, M., *Trans. Inst. Chem. Engrs.*, **24**, 90-101 (1946).

fractions were substituted for technical benzol, it was found advantageous to pass the dephenolizer effluent through sand filters to reduce the loss of solvent. The results of some laboratory and pilot-plant experiments on phenolic liquid wastes from carbonization of American coals, spon-



(Courtesy, International Chemical Engineering & Process Industries)

FIGURE 31. Phenol extraction plant

sored in the United States by the Koppers Company, Inc., appear to confirm the conclusions of the European investigators as to the value of adding small amounts of certain higher aromatic nitrogenous bases to certain extraction solvents when used for the removal of phenol from waste liquors.

(2) Adsorption on Solid Media. A number of dephenolization processes

based on the application of solid adsorbents to recover the phenol from the still wastes have been proposed. Extensive investigations on the use of activated carbon to remove phenol from crude ammonia liquors have been described by Sierp.¹⁸⁶ A large industrial installation of this type of phenol recovery plant was made in 1930 by Lurgi at a high-temperature coke-works in the Ruhr District of Germany. Coke filters were used to clarify the waste liquors, and their phenol contents were then adsorbed by beds of activated carbon, which when first used, removed phenol down to 0.05 g/l. Several advantages were claimed for the process, but when the price of phenol dropped, the plant was shut down and had not been reactivated by 1947. Possible reasons for closing the plant, as given by Rhodes,¹⁷¹ are as follows: "(a) The process was not continuous; (b) reactivation of the carbon was difficult owing to the accumulation of high boiling acidic and tarry constituents; and (c) plants had already been constructed for working up phenolates from the Pott-Hilgenstock, steam stripping, and other processes." Research by Tesi²¹⁰ indicated the possibility that activated carbon might be applied in a post-dephenolization process.

(3) Vapor-Phase Dephenolization. Vapor-phase dephenolization is well illustrated by the Koppers steam recirculation dephenolizer developed in the United States during 1925-28, under patents issued to Shaw.¹⁸⁰ In this process the phenol in the ammonia still waste liquor is swept out with steam and the steam-phenol vapor is contacted in the top section of a saddle packed vapor-absorption column with a countercurrent spray of sodium hydroxide, which reacts with the phenol to form sodium phenolate (p. 398). The sodium phenolate collects in the bottom section of the reaction column and is drawn to storage tanks from which it may either be sold as the phenolate or be pumped to the springing column in which the phenol is liberated, usually by reaction with the carbon dioxide. A comparatively pure grade of crude phenol is produced by this type of dephenolizer. The steam is recirculated, the make-up steam requirements are said to be small. A flow diagram of this type of dephenolization process is given in Figure 32, and its operation has been discussed by Wilson.²³² There are more of the Koppers Vapor-Phase, or steam-stripping dephenolizers, and variations of the benzene extraction process in operation in the United States and Europe than of any of the other types. The construction and operation of each type have been well described by Gollmar^{79a} and by Wilson and Wells.⁶⁻²⁵ However, in England and other European countries there are or have been installations of all the different dephenolization processes mentioned.

The efficiencies of dephenolization processes for recovering the phenol in the liquid wastes depend on the design, construction, and operation

of the dephenolizer. Installations of any of the processes briefly outlined are usually made so as to remove from 88 to 93 per cent of the phenol from the waste liquors. Practical problems in the operation of equipment for the disposal of wastes from an integrated steel plant and by-product coke works have been discussed by Bundy and Jordan.³⁰ Dephenolization systems can be designed and constructed so that by very careful operation, removals of phenol up to around 95 to 97 per cent can be attained, but the costs of construction and operation rise very rapidly for dephenolizers designed to remove more than around 93 per cent of the phenol in the waste liquors fed to the dephenolizer. Results of analyses made by the Koppers Company's Fellowship at Mellon Institute have shown

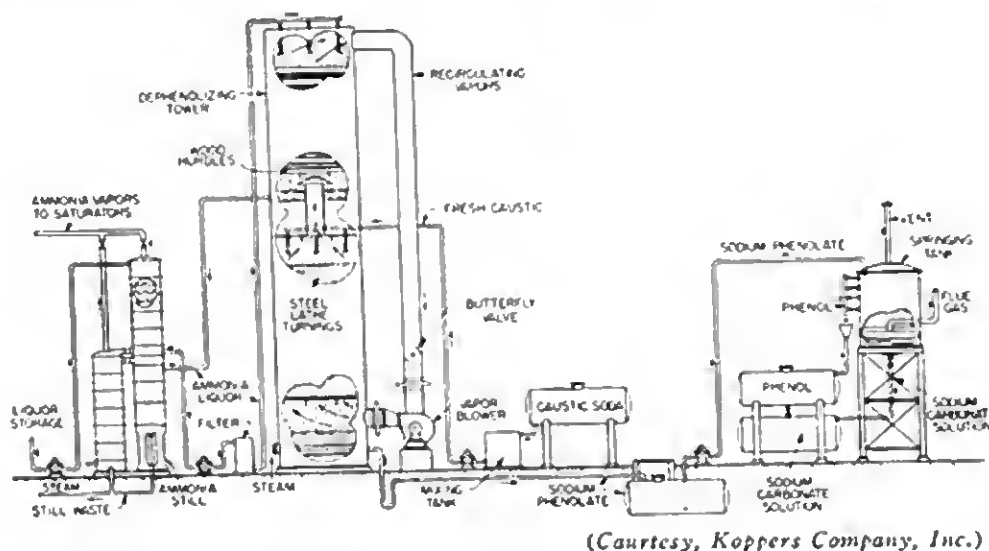


FIGURE 32. Flow diagram of Koppers vapor phase dephenolizer for recovery of phenol from by-product coke plant waste liquor

the phenol contents of the feed liquors to the dephenolizers may range from around 1,500 to 3,500 ppm, and of the dephenolizer effluents, usually from about 100 to 300 ppm. Analyses of seven different samples of the effluent from a specially designed and constructed Koppers steam-recirculation dephenolizer installed several years ago at a large by-product coke plant ranged from 11 to 35 ppm, but the costs of construction and operation of such a dephenolizer are high. Under these conditions, much research has been directed in recent years toward the development, if possible, of a reasonably priced post-dephenolization process.

Methods for Post-Dephenolization of Dephenolizer Effluents. In recent years there has been considerable agitation to still further reduce the quantities of phenol being discharged to waterways, especially if they are used farther downstream as sources of municipal water supplies.

An upper limit of 5 ppb of phenol when dispersed in the receiving watercourse has been specified in some cases. Since the costs for design, construction, and operation of dephenolizers to remove 99+ per cent of the phenol contents of industrial waste liquors would be prohibitively high, researches have been initiated to develop technically sound and, as nearly as possible, economically satisfactory post-dephenolization processes. Some of the methods being investigated are the following: (1) adsorption of the phenol on solid materials; (2) the use of ion-exchange resins; (3) burning or catalytic oxidation; (4) aeration; (5) ponding; (6) biological treatments; (7) applications of chemicals, such as chlorine, chlorine dioxide, ozone, and manganese compounds; and (8) combinations of one or more of these methods.

Methods are being investigated on the application of activated carbon and some other solid adsorbents to remove the relatively small amounts of phenol which remain in dephenolizer effluents, even though the use of such materials has not proved to be generally satisfactory in primary dephenolizers.²¹⁰ The dephenolizer effluents usually contain less of tarry and gummy materials than are often present in the crude ammonia still wastes and which reduce the useful life of solid adsorbents. Also, some manufacturers are now producing adsorbents which are said to have much better properties for recovery of phenol than those previously available. Results of exploratory experiments with some activated carbons showed practically complete removal of phenol from the waste liquor when sufficient amounts of the adsorbents were applied, but the costs might be high.

Investigations on the use of ion-exchange resins for recovering phenol from waste liquors are reported to have given favorable results in some cases, but there has been no general adoption of this method.

The possibility of burning the phenol by spraying the liquid wastes into hot furnace or stack gases has been considered. A catalytic oxidation process developed by E. I. du Pont de Nemours and Company, Inc., has been described by Moses and Green.¹⁴⁹ It proved useful on a pilot-plant scale for destroying small quantities of organic compounds in small and in large volumes of liquid wastes, for which no other satisfactory method of disposal could be found.

Aeration of the waste liquors has reduced the phenol contents and oxygen demands of the waste liquors in some investigations, but the time-rates of such reductions by simple aeration were too slow for most practical purposes.

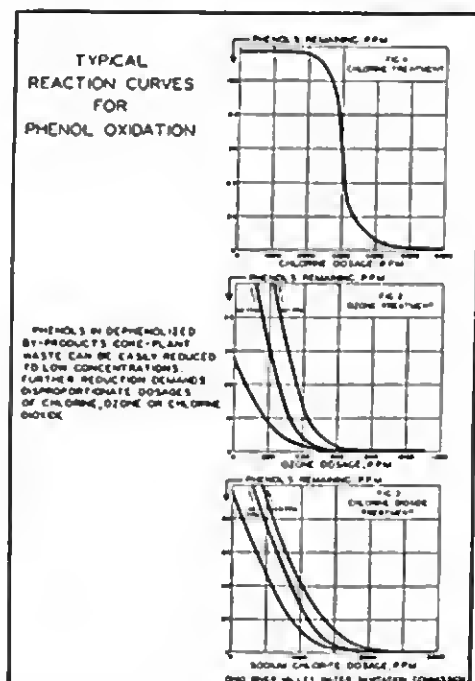
Ponding of the dephenolizer effluents has been considered for coke plants where sufficient areas of favorable topography are available for the construction of storage ponds or lagoons. Experiments conducted by

Bach¹² showed that when 10 ppm of phenol was added to the water in a vat of 210 liters capacity, only a trace of phenol remained after four days. In similar tests with phenol concentrations up to 25 ppm, the phenol was rapidly destroyed. There appeared to be no harmful effects to the goldfish in the water containing 10 ppm of phenol. In an investigation on the removal of phenol and the three cresols from samples of natural water from several rivers in Ohio and Michigan, Ettinger and Ruchhoft^{68,69} added 1,000 ppb of the phenols to the samples and found that the phenol usually disappeared in from 5 to 7 days, but from 10 to 16 days elapsed before all of the cresols had wholly disappeared. The experiments were conducted at 4° and 20°C. Dissimilation of the phenolic substances proceeded more rapidly at 20°C, and temperature was one of the most important factors in governing the rates of the microbiological activities. Other factors of importance were: The microorganisms which attack phenols must be in the medium or it must be inoculated, and the required amounts of assimilable minerals, phosphates and nitrogenous substances must be present. Judging from the results mentioned, if the dephenolizer effluents were diluted to phenol contents of 1 to 10 ppm, the use of storage ponds having the necessary capacity to permit the residence time required before the liquid wastes were discharged to the receiving watercourse, might be a satisfactory method of disposal. Seeding from time to time with sewage or cultures of phenol-destroying microorganisms and additions of the required mineral salts and nutrients would probably be necessary to attain the best results. Aeration and bacterial oxidation, with addition of phosphates to promote bacterial growth, is reported by Rhodes¹⁷¹ to have been applied by the *Emsehergenossenschaft* and other organizations in Germany to destroy the phenol in coke plant liquid wastes. It is not generally used as a primary dephenolization operation, but usually as a polishing dephenolization treatment of waste waters already partially dephenolized. The use of bacterial beds for destroying phenols is widely applied in Great Britain especially as a finishing treatment. The disposal of phenolic waste liquors into surface lagoons, underground caverns, or abandoned coal mines has not been a generally satisfactory practice in the United States.

Biological treatment in municipal sewage plants of by-product coke works' liquid wastes containing phenol and cresols has proved satisfactory in some cases where the volume of sewage is sufficient to dilute the phenolic wastes to a concentration of not over 20 to 30 ppm in the mixture, which should also be practically free of toxic substances, as previously stated. Proper operation of a well designed and constructed dephenolizer will remove 90 per cent or more of the phenol in the still wastes and, in doing so, it also markedly reduces the oxygen demand of

the effluent. Hence, the added load on a sewage plant is much less than if the waste liquors had not been dephenolized. However, many by-product coke plants are located in places where there are no municipal sewage plants, and other methods for post-dephenolization have to be considered.

Applications of chemicals to destroy the phenols in the waste liquors have been extensively investigated. An outstanding cooperative investigation along these lines was carried on at the by-product coke plant



(Courtesy, Ohio River Valley Water Sanitation Commission)

FIGURE 33

of the Armeo Steel Corporation in Hamilton, Ohio. Other cooperating private companies which supplied equipment, chemicals and technical assistance were as follows: Wallace and Tiernan supplied the chlorine; an ozonizer was furnished by the Ozone Process Division of Welsbach Corporation; and the Mathieson Chemical Corporation contributed the chlorine dioxide. Public agencies which cooperated with the consulting services of experts and with laboratory personnel were: The U.S. Public Health Service; the Ohio State Health Department; and the entire project was organized and coordinated by the staff of the Ohio River Valley Water Sanitation Commission. A preliminary paper outlining this project was presented by Cleary and Kinney¹⁰ and a bulletin covering the complete investigation has been issued by the Commission.¹⁰² The results of the laboratory and pilot-plant researches showed that the phenols in the dephenolizer effluent, ranging in concentrations

from 28 to 332 ppm, could be destroyed by applications of sufficient quantities of chlorine, ozone, or chlorine dioxide. The rates of removal of the phenol by the different reagents are shown by the typical reaction curves for phenol oxidation (Figure 33). The oxygen consumed (OC) values of the dephenolizer effluent, as determined by the dichromate reflux method, varied from 1,400 to 1,800 ppm, about one-half of which was due to the chlorides in the waste liquor, which ranged from 7,000 to 9,700 ppm. The 5-day biochemical oxygen demands (BOD) varied from 300 to 400 ppm. The OC and BOD values were reduced over 60 per cent by each of these oxidants. The phenol contents were determined by a variation of the 4-aminoantipyrine method which gives excellent checks on the Gibbs Method^{20,6-20} down to a defined level and required only about 45 minutes as compared to the 18 hours often necessary for a phenol analysis by the Gibbs procedure. Many methods of analysis for phenol are available and, in the author's experience with several different methods, there was no difficulty in obtaining good check results when analyzing comparatively pure solutions. However, when analyzing complex industrial waste liquors for their phenol contents by different methods, wide differences in data may result unless the interfering substances are first removed and a suitable method of analytical procedure is followed. The importance of screening out the interfering materials has been discussed by Ettinger and Kroner.⁷⁰ Many analyses were made of the principal constituents in the dephenolizer effluent and of the liquors after the treatments. The flow diagrams for the different treatment processes are given,¹⁶² but the technical and comparative costs factors for the three processes, chlorine, ozone, and chlorine dioxide, would have to be developed specifically for each plant where the installation of a post-dephenolization process is being considered.

Combinations of Two or More of the Methods. The use of other oxidizing compounds such as potassium permanganate, sodium dichromate, and sodium peroxide to destroy the phenols in trade wastes has been investigated, but the costs were too high for industrial practice, and there were other objectionable factors. Good results on the oxidation of the phenols in the waste liquors from the carbonization of brown coal by a combination of aeration and applications of crushed pyrolusite have been reported by Ruff and Martynova.¹⁷⁶ In the laboratory experiments the manganese ores were said to act as catalysts for the added atmospheric oxygen and also served as good oxidizing agents. A process based on the application of manganese dioxide to destroy phenol has been patented by Wells and Wilson.²³⁰ Other examples of applications of two or more methods to remove the phenols from waste liquors have been given

in several of the processes previously described. Researches are in progress to develop new or improve present processes for further reducing the phenol contents of industrial waste liquors. Under present conditions, if the waste liquor contains 400 ppm of phenol and is large in volume, it would probably be advisable to install a good dephenolizer as the primary operation for phenol removal, unless mutually satisfactory arrangements can be made with the officials of a large, conveniently located municipal sewage treatment plant, as is done in the Sanitary District of Chicago, Illinois. The receipts from the sale of the crude phenol recovered by the dephenolizer seldom affords an over-all profit, except possibly in large by-product coking plants. However, most operators of by-product coke plants, from the standpoint of public relations, would be satisfied if they could break even financially on the dephenolizer installations and operations. In England and Germany the disposal of gasworks and by-product coke plant phenolic waste liquors along with municipal sewage has been a quite common practice for many years. To destroy the small quantities of phenol remaining in dephenolizer effluents and present in some other industrial wastes, consideration should be given to the relative advantages and disadvantages of the several methods which have been briefly outlined: the treating of the liquid wastes in a municipal sewage plant; installation at the coke works of an aerobic biological treatment unit, such as a trickling filter or an activated sludge system; and renewed attention which is being given to the possible use of bacterial filters. Filters of this type were developed early in England by Frankland and Silvester,⁷⁷ and Fowler and associates,^{73,74,75} and in the United States by Brown;²⁹ and there was one large-scale installation in Germany, in the Emscher District. According to Sperr,¹⁹⁵ the operation of large bacterial filters is expensive, but this method of treatment would be applicable under conditions where most of the phenol has been removed by a dephenolizer or other method, where the last traces of phenol must be eliminated, and where no municipal or other sewage treatment plant is available.

In reviewing the many methods for removal of phenols from still wastes or other effluents to a point where there would be little danger of its causing unpleasant tastes or odors in the downstream public water supplies, it appears that the following general procedures might be followed. If there is a high content of phenol in the waste liquor, treat it in a suitably designed and constructed dephenolizer and discharge the dephenolizer effluent to a municipal sewage treatment plant, provided the volume and quality of the sewage is such that the residual phenol can be readily destroyed by biological activity. If no such sewage plant is available, a waste liquor containing not more than 200 to 300 ppm

of phenol might be treated by the coal adsorption process to reduce the phenol content to around 20 to 30 ppm and then be given a final treatment on a trickling filter or possibly by one of the chemical oxidation methods with chlorine, chlorine dioxide, or ozone. Comparative data on capital investment required, and operation and maintenance costs would have to be considered, since they vary in different sections of the country. The use of bacterial beds as a polishing treatment is apparently quite often used in Great Britain and in parts of continental Europe. No general procedure can be recommended for all plants, but the phenol disposal problems in each gasworks or by-product coke plant must be considered in relation to available sewage treatment plants, volume of flow in the receiving waterway, and whether or not the water is used for potable supplies farther downstream. Factors such as regional topography, state laws and municipal ordinances must also be considered, as well as the usual economic factors, in order to arrive at the most satisfactory solution to any specific problem in the disposal of phenolic waste waters.

References

1. American Petroleum Institute, Manual on Disposal of Refinery Wastes, Sect. I, 13-36 (1949).
2. Ash, S. H., *Min. Met.*, 22, No. 411, 167-71 (Mar. 1941); *U.S. Bur. Mines Inform. Cir. 7175* (June 1941).
3. *Ibid.*, *U.S. Bureau Mines Bull.*, 494, 27 pp. (1950).
4. Ash, S. H., Eaton, W. L., Hughes, K., Romischer, W. M., and Westfield, J., *U.S. Bur. Mines Tech. Paper*, 727, 78 pp. (1949).
5. Ash, S. H., Felegy, E. W., Kennedy, D. O., and Miller, P. S., *U.S. Bur. Mines Bull.*, 508, 72 pp. (1951).
6. Ash, S. H., Eaton, W. L., Gilbert, J. C., James, H. M., Jenkins, H. E., Kennedy, D. O., Kynor, H. D., Link, H. B., and Romischer, W. M., *U.S. Bur. Mines Rept. Invest.*, 4700 (1950).
- 6a. Ash, S. H., Doherty, R. E., Miller, P. S., Romischer, W. M., and Smith, J. D., *U.S. Bur. Mines Bull.*, 513 (1952).
7. Aston, R. N., *J. Am. Water Works Assoc.*, 42, 151-4 (1950).
8. Audas, F. G., British Patent 653,317 (1948), assigned to Audas and Thompson, Ltd.
9. Austin, R. J., and Vause, E. H., *Proc. Sixth Ind. Waste Conf., Purdue Univ.*, 272-77 (1951).
10. Bach, H., *Z. Angew. Chem.*, 39, 1093-8 (1926).
11. ———, *Gas- u. Wasserfach*, 69, 912-5; 923-5; 947-51 (1926).
12. ———, *Gesundh. Ing.*, 51, 773-4 (1928).
13. ———, *Gas- u. Wasserfach*, 72, 375-7 (1929).
14. ———, *Gesundh. Ing.*, 52, 796 (1929).
15. ———, *Gesundh. Ing.*, 53, 790-2 (1930).
16. ———, *Proc. Third Inter. Conf. Bituminous Coal*, Vol. II, 924-59 (1931).
17. ———, *Water Works & Sewerage*, 84, 389-93; 446-9 (1937).

18. Bach, H., and Uthe, H., *Brennstoff-Chem.*, 8, 120-1 (1927).
19. Bardwell, R. C., *Ry. Eng. and Maintenance*, 30, 9, 476-9 (1934); and private communications.
- 19a. Bartels, R., *Zentr. Bakt. Parasitenk.*, II Abt., 103, 1-38 (1940).
20. Baylis, John R., *J. Am. Water Works Assoc.*, 19, 597-604 (1928).
21. Bescher, R. H., *Proc. Am. Wood-Preserver's Assoc.*, 145-8 (1945).
22. Bilharz, O. W., *Trans. Am. Inst. Min. Met. Eng.*, 181, 282-291 (1949).
23. Bottoms, R. R., U.S. Patent 1,783,901 (1930)
24. ———, *Ind. Eng. Chem.*, 23, 501-4 (1931).
25. Bragg, G. A., U.S. Patent 1,920,626 (1933).
26. Braley, S. A., *Min. Eng.*, 111, No. 8 (Aug. 1951); *Trans. Am. Inst. Min. Eng.*, 190, 703-707 (1950).
27. ———, private communication (1952).
28. Braley, S. A., Bcal, G. D., and Levy, R. S., *Bull. Sanitary Water Board, Pa. Dept. of Health* (April 1951).
29. Brown, Ralph L., U.S. Patent 1,437,394 (1922), assigned to Koppers Co., Inc.
30. Bundy, K. N., and Jordan, P. E., *Sewage Works J.*, 21, 694-9 (1949); *Iron Steel Engr.*, 26, No. 4, 79-86 (1949).
31. Burke, S. P., and Downs, R., *Am. Inst. Min. Met. Engrs. Tech. Pub.* 79, 20 pp. (1937).
32. Buswell, A. M., *Water and Sewage Works*, 96, 115-6 (1949).
33. Campbell, J. R., *Coal Mine Management*, 2, No. 6, 25-31 (1923).
34. Carbonc, W. E., *Sewage and Ind. Wastes*, 22, 200-5 (1950).
35. Carpenter, L. V., *W. Va. Univ. Eng. Expt. Sta. Tech. Bull.* 2, 27-36 (Nov. 1928).
36. Carpenter, L. V., and Davidson, A. H., *Proc. W. Va. Acad. Sci.*, 4, 93-99 (1930).
37. Carpenter, L. V., and Herndon, L. K., *W. Va. Univ. Eng. Expt. Sta. Res. Bull.* 10, 38 pp. (1933).
- 37a. Carvlin, G. M., *Natl. Petroleum News*, 30, 268-74 (1938).
38. Chamberlin, Noel S., and Griffin, A. E., *Sewage and Ind. Wastes*, 24, No. 6, 750-63 (June 1952).
39. Clark, G. J., *Trans. Min. Met. Eng.*, 177, Coal Division 95-112 (1948)
40. Cleary, E. J., and Kinney, J. E., *Proc. Sixth Ind. Waste Conf.*, 1951, 158-70, Purdue Univ.
41. Coal Resources of the World, Twelfth International Geological Congress, Toronto, Canada (1913).
42. Coburn, S. E., *Sewage Works J.*, 21, 522-4 (1949).
43. Colmer, A. R., and Hinkle, M. E., *Science*, 106, No. 2751, 253-56 (Sept. 1947).
44. Colmer, A. R., Temple, K. L., and Hinkle, M. E., *J. Bact.*, 59, 317-28 (1950).
45. Cooper, E. A., *J. Soc. Chem. Ind.*, 66, 48-50 (1947)
46. Corps of Engineers U.S. Army, "The Ohio River," 5th Ed. (1935).
47. Coxon, W. F., *Gas Times*, 54, 42 (1948).
48. Crawford, R. M., *Ind. Eng. Chem.*, 18, 313-15 (1926).
49. ———, 19, 168-9 (1929)
50. ———, 19, 966-8 (1927).
51. Crichton, A. B., *Trans. Am. Inst. Min. & Met. Engrs.*, 69, 434-46 (1923).
52. ———, *Trans. Am. Soc. Civil Engrs.*, 92, 1332-42 (1928).
53. ———, *Mining Congress J.*, 12, 418-20 (1926)
54. Crohurst, H. R., *U.S. Pub. Health Service Bull.* 204 (1933).
55. Czckalowski, J. W., and Skarzynski, B. J., *Gen. Microbiol.*, 2, 231-8 (1948).
56. Davis, D. E., *Eng. News Record*, 117, 586-7 (1936).

57. Denig, F., *Am. Gas Assoc. Proc.*, **15**, 903-12 (1933).
58. ———, *Iron Steel Eng.*, **15**, No. 10, 32-53, 63 (1938).
59. Dierichs, A., U.S. Patent 2,415,087 (1947).
60. ———, *Chem. Tech.*, **15**, 144-5 (1942).
61. ———, *Chem. Tech. (Berlin)*, **2**, 79-83 (1950).
62. Downs, W. S., *W. Va. Univ. Eng. Expt. Sta. Res. Bull.* **13**, 68 pp. (Dec. 1934).
63. Drake, C. F., *J. Am. Water Works Assoc.*, **23**, 1261-71 (1931).
64. Eavenson, H. N., *Coal Age*, **40**, 195-6, 210 (1935).
65. ———, *Trans. Am. Inst. Mining Met. Engrs.*, **66**, 624-35 (1921-2); *Mining Metallurgy 1921*, No. 169, p. 30.
66. ———, *Trans. Am. Inst. Mining Met. Engrs. (Coal Division)*, **168**, 14-26 (1946).
67. Ellms, J. W., and Lawrence, W. C., *J. Am. Water Works Assoc.*, **9**, 463-73 (1922).
68. Ettinger, M. B., and Ruchhoft, C. C., *Anal. Chem.*, **20**, 1194-6 (1948).
69. ———, ———, *Ind. Eng. Chem.*, **41**, 1422-7 (1919).
70. Ettinger, M. B., and Kroner, R. C., *Proc. Fifth Ind. Waste Conf., Purdue Univ., Eng. Bull. Extension Series No. 72*, 345-59 (Nov. 29-30, 1950).
71. Evans, W. C., *Biochem. J.*, **41**, 373-382 (1917).
72. Felegy, E. W., Johnson, L. H., and Westfield, J., *U.S. Bur. Mines Tech. Paper*, **710**, 49 pp. (1918).
73. Fowler, G. J., Ardern, E., and Lockett, W. T., *J. Soc. Chem. Ind. (London)*, **30**, 174-79 (1911).
74. Fowler, G. J., and Holton, A. L., *J. Soc. Chem. Ind. (London)*, **30**, 180-8 (1911).
75. Fowler, G. J., and Shepherd, S. W., *J. Soc. Chem. Ind. (London)*, **30**, 184-4 (1911).
76. Francis, C. B., U.S. Patent 2,416,744 (1947).
77. Frankland, P. F., and Silvester, H. J., *J. Soc. Chem. Ind.*, **26**, No. 6, 234-7 (1907).
78. Giles, R. N., Scheineman, F. W., Nicholson, C. T., and Austin, R. J., *Sewage and Ind. Wastes*, **23**, No. 3, 281-94 (1954).
79. Gollmar, H. A., *Ind. Eng. Chem.*, **26**, 430-2 (1934).
- 79a. *Ibid.*, **39**, 596-601 (1947).
80. Gollmar, H. A., *Steel*, **127**, No. 3, 102-3 (1950).
81. Gray, P. H. H., and Thornton, H. G., *Centr. Bakt. Parasitenk II*, Abt. 73, 74-96 (1928).
82. Griffith, E., *Trans. Am. Inst. Mining Met. Engrs.*, **168**, 127-141 (1946).
83. Gross, C. D., and Lee, C., *Proc. Sixth Ind. Waste Conf.*, 10-21, Purdue Univ., (1951).
84. Gutzeit, G., *Sewage Works J.*, **21**, 91-99 (1949).
85. ———, *Chem. Engr. Progress*, **46**, 335-42 (1950).
86. ———, *Petroleum Processing*, **7**, No. 6, 828-32 (1952).
87. Harlow, I. F., Powers, T. J., and Ehlers, F. A., *Sewage Works J.*, **10**, 1013-59 (1938).
88. Harlow, I. F., and Powers, T. J., *Ind. Eng. Chem.*, **39**, 572-7 (1947).
89. Hatch, B. F., *Blast Furnace Steel Plant*, **17**, 1797-1800 (1929); **18**, 296-8; 648-9 (1930).
90. ———, *Ind. Eng. Chem.*, **21**, 431-3 (1929).
91. ———, *Water Works and Sewerage*, **81**, 99-100 (1934).
92. ———, *Ohio Conf. Sewage Treatment Fifth Annual Rept. 1931*, 46-52 (1932).
93. Hebley, H. F., *Paper Annual Meeting of the W. Va. Sewage Ind. Wastes Assoc.*, 1949.
94. Herndon, L. K., *W. Va. Univ. Eng. Expt. Sta. Tech. Bull. No. 4*, 115-42 (1931).

95. Herndon, L. K., Ch. E. Thesis, W. Va. Univ. (1934).
96. Herndon, L. K., and Hodge, W. W., *W. Va. Univ. Eng. Expt. Sta. Res. Bull.* 14, 43 pp. (1936); *Proc. W. Va. Acad. Science*, 9, 39-61.
97. Hinkle, M. E., and Koehler, W. A., *Tech. Pub. No. 2351, Class F, Coal Tech., Am. Inst. Min. Met. Eng.* (May 1948).
98. Hoak, R. D., *Ind. Eng. Chem.*, 39, 614-18 (1947).
99. ———, U.S. Patent 2,529,874 (1950).
100. Hodge, W. W., *Ind. Eng. Chem.*, 29, 1048-55 (1937).
- 100a. *Ibid.*, 31, 1364-81 (1939).
101. Hodge, W. W., *W. Va. Univ. Sci. Assoc. Bull.* 1, No. 4, 35-43 (1924).
- 101a. ———, *W. Va. Univ. Expt. Sta., Tech. Bull.* 1, 40-54 (1927).
102. ———, *W. Va. Univ. Eng. Expt. Sta. Res. Bull.* 18, p. 30 (1938).
103. Hodge, W. W., and Herndon, L. K., *W. Va. Eng. Expt. Sta. Tech. Bull. No. 5*, 48-62 (1932).
104. Hodge, W. W., and Hinkle, M. E., *Paper Div. Water, Sewage Sanit. Chem., Am. Chem. Soc.*, Spring meeting (April 1946).
105. Hodge, W. W., and Niehaus, E. J., *W. Va. Univ. Eng. Expt. Sta. Res. Bull.* 15, 30 pp. (1936).
106. Hodge, W. W., and Newton, R., *W. Va. Univ. Expt. Sta. Tech. Bull.* 7, 52-69 (1934).
107. Hodge, W. W., and Tallon, G. R., unpublished data. Koppers Company, Inc., Effluents Treatments Fellowship, Mellon Institute of Industrial Res.
108. Hodge, W. W., Koehler, W. A., and Hinkle, M. E., *Paper Div. Water, Sewage, Sanit. Chem., Am. Chem. Soc.*, Fall meeting (1946).
109. Hoffert, J. R., *Ind. Eng. Chem.*, 39, 612-6 (May 1947).
110. ———, *Proc. Fifth Ind. Waste Conf., Purdue Univ.* (1949).
111. Holmquist, C. A., *Am. J. Pub. Health*, 19, 819-20 (1929).
112. Howard, N. J., *Eng. Contract. Rec.*, 58, 86, 88, 90 (1945).
113. Jacobson, D. L., *Gas Age Record*, 63, 597-600 (1929).
114. Jones, H. E., *W. Va. Univ. Eng. Expt. Sta. Tech. Bull.* 1, 31-9 (1927); *Chem. & Met. Eng.*, 35, 215-8 (1928).
115. Kameda, Y., and Toyoura, E., *J. Pharm. Soc.*, 67, 1-2 (1947).
116. Kaplan, B. B., *Proc. W. Va. Acad. Sci.*, 4, 90-2 (1930).
117. Kaplan, B. B., and Reger, D. B., U.S. Patent 1,878,525 (1932).
118. Kastens, M. L., and Barraclough, Ronald, *Ind. Eng. Chem.*, 43, No. 9, 1882-92 (1951).
119. Key, A., *The Surveyor*, 81, 335-7 (1932).
120. Knight, J. J., private communications (1951).
121. Kohman, E. F., *Ind. Eng. Chem.*, 15, 518 (1923).
122. Koons, C., Paper Production and Chemical Conf., Am. Gas Assoc. (May 1952).
123. Koppers Company, Inc., British Patent 605,635 (1918).
- 123a. Kramer, N., and Doetsch, R. N., *Arch. Biochem.*, 26, 401-5 (1950).
124. Leathen, W. W., and Madison, K. M., *Abst. of Papers, Soc. Am. Bacteriologists*, 1949, p. 64.
125. Leathen, W. W., and Braley, S. A., *Bact. Proc.*, 1950, Abst. of Papers, pp. 21-2.
126. ———, ———, *Bact. Proc.*, 1951, Abst. of Papers, pp. 21-2.
127. Leathen, W. W., McIntyre, Lois D., and Braley, S. A., *Bact. Proc.*, 1952, Abst. of Papers, p. 15.
128. ———, ———, ———, *Science*, 114, No. 2959, 280-1 (Sept. 14, 1951).
129. Leitch, R. D., *Paper Am. Inst. Min. Met. Engrs.* (Feb. 1937)

130. Leitch, R. D., *U.S. Bur. Mines, Repts. Invest.*, 2725 (1926); 2889 (1928); 2895 (1928); 3119 (1931); 3102 (1931); 3097 (1931); 3098 (1931); 3146 (1932).
131. ———, *Pub. Health Rept.*, 40, 2021-26 (1925).
132. ———, *Mining Cong. J.*, 14, 835-9, 848 (1928).
133. Leitch, R. D., and Yant, W. P., *Coal Age*, 35, 78-80 (Feb. 1930).
134. Leitch, R. D., Yant, W. P., and Sayres, R. R., *U.S. Bur. Mines, Repts. Invest.*, 2994 (1930).
- 134a. Lesser, W. H., *U.S. Bur. Mines, Repts. Invest.*, 4656 and 4749 (1950).
135. Lowenstein-Lom, W., Schnabel, B., and Kejla, V., *Gaz. Woda i Tech. Sanit.*, 24, 94-9 (1950).
136. Lowenstein-Lom, W., *Inter. Chem. Eng. and Proc. Ind.*, 32, No. 5, 216-19 (1951).
137. Lowy, A., "Coal Products Chart," New York, D. Van Nostrand Co. (1923).
138. Lutz, W. S., and Griffith, J. T., *Trans. Am. Inst. Min. Met. Engrs.*, 168, 145-54 (1946).
139. Lyon, E. W., private communications (1950, 1952).
140. Marsden, A., *Gas World*, 133, No. 3481, 524-7, No. 3487, 653-6; 672-7 (1951).
141. Mathews, W. W., *Sewage and Ind. Wastes*, 24, No. 2, 164-80 (1952).
142. Maurer, M. H., and Roberts, E. S., U.S. Patent 2,605,171 (July 29, 1952).
143. Milwaukee Sewerage Commission, Seventh Annual Rept. (1920).
144. Mohlman, F. W., *Am. J. Pub. Health*, 19, 145-56 (1929).
145. ———, *Sewage Works J.*, 19, 473-7 (1947).
146. Monkhouse, A. C., *Chemistry & Industry*, 58, 596-600 (1939).
147. Morgan, L. S., Paper presented at Annual Meeting Penna. Sewage and Industrial Wastes Assoc. (Aug. 1952).
148. Moses, D. V., and Mackey, B. H., *Am. Gas J.*, 137, No. 2, 21-3 (1932); *Chem. and Met. Eng.*, 39, 441-3 (1932).
149. Moses, D. V., and Green, R. W., *Chem. Eng. News*, 29, No. 18, 1734 (Apr. 30, 1951).
150. Murdoch, D. G., and Cuckney, M., *Trans. Inst. Chem. Engrs.*, 24, 90-101 (1916).
151. ———, ———, *British Coal Util. Res. Assoc.*, 11, No. 2, 53 (1947).
152. Nellist, G. R., *Gas World*, 135, No. 3516, Supplement 7-13 (Jan. 5, 1952).
153. Nelson, H. W., Snow, R. D., and Keyes, D. B., *Ind. Eng. Chem.*, 25, 1355-8 (1933).
154. Nelson, W. L., and Hall, E. P., private communication (1952).
155. Nieklin, T., *Gas World*, 128, 300-3 (1948).
156. Nolte, E., *Beitr. Wasser-Ab. Wasser u. Fischerei Chem.*, 1947, p. 3.
157. ———, *Deut. Landeskultur-Ztg.*, 7, 14 (1938).
158. Nolte, E., and Boudt, H. J., *Chem. Zentr.*, 1, 549 (1947).
159. Nolte, E., Meyer, H. J., and Fromke, E., German Patent 683,148 (1939).
160. Ohio River Pollution Survey, Final Report to the Ohio River Committee, Supplement "C," Acid Mine Drainage Studies. Federal Security Agency, United States Public Health Service (1942).
- 160a. Ohio River Pollution Control, Part Two (1944).
161. Parton, W. J., *Ind. Eng. Chem.*, 39, 646-52 (1947).
162. Phenol Wastes: Treatment by Chemical Oxidation. Ohio River Valley Water Sanitation Commission (June 1951).
163. Phillips, O. B., Paper presented before Blast Furnace and Coke Oven Association of the Chicago District, Joliet, Ill. (June 3, 1931).
164. Powell, A. R., *A. G. A. Proc.* (1929).
- 161a. ———, *Gas Age-Record*, 77, 711-15, 720 (1936).

165. Powell, A. R., *Ind. Eng. Chem.*, **31**, 789-96 (1939).
166. ———, *Natl. Petroleum News*, **29**, No. 24, 50-8 (1937).
167. Powell, A. R., and Parr, S. W., *Univ. Ill. Eng. Expt. Sta. Bull.*, **111**, pp. 66 (1919).
168. Powers, T., *Sewage Works J.*, **17**, 330-7 (1945).
169. Preston, E., *Blast Furnace Steel Plant*, **34**, 121-5 (1946).
170. Purdy, W. C., *U.S. Pub. Health Service Bulls.*, **131** (1923); **198** (1930).
171. Rhodes, E. O., *U.S. Bur. Mines, I. C.*, **7409**, 76, 87 (Sept. 1947).
172. *Ibid.*, **7490**, 36-41 (Feb. 1949).
173. Roberts, T. P., *Engrs' Soc. West. Penn.*, **27**, 375-451 (1911).
174. Roos, G. A., *Mining Congr. J.*, **31**, No. 6, 32-34, 50 (June 1945)
- 174a. Rosenstein, L., and Kramer, G. A., U.S. Patent 1,945,163 (1934).
175. Rudolfs, W., *Sewage Works Eng. and Munic. Sanit.*, **16**, 501-2 (1945).
176. Ruff, W. T., and Martynova, O. I., *Vodos, Sanit. Tekh.*, **15**, 98 (1940); *Water Pollution Res.*, **20**, 237 (1947).
177. Salvati, R., Discussion of H. N. Eavenson Paper (Ref. 66).
- 177a. Scollon, J. A., *Meehanization*, **15**, No. 10, 105-9 (Oct. 1951).
178. Sechrist, W. D., and Chamberlin, N. S., *Proc. Sixth Ind. Waste Conf., Purdue Univ.* 396-412 (Feb. 21-23, 1951).
179. Shaw, J. A., U.S. Patent 2,028,124-5 (1936).
180. ———, U.S. Patents 1,928,507 (1933); 1,956,597 and 1,957,295 (1934).
181. Shelford, V. E., Illinois State Lab., *Nat. History XI*, Art. VI, 381-412 (1917).
182. ———, *J. Am. Water Works Assoc.*, **5**, 437-47 (1918).
183. ———, *J. Am. Pharm. Assoc.*, **7**, 597-603 (1918).
184. Shelford, Wells, Forbes, and Richardson, Illinois State Lab., *Nat. History XII*, Art. VI, 1092 (1919).
- 184a. Shnideman, L., and Bowman, L. B., *Gas Age-Record*, **61**, 626-8, 634 (1928).
185. Siebert, C. L., Jr., *Proc. Sixth Ind. Waste Conf.*, pp. 253-71, Purdue Univ. (Feb. 1951).
186. Sierp, F., *Gas- u. Wasserfach*, **76**, 105-9 (1933).
187. Sisler, J. D., Fraser, T., and Ashmead, D. C., *Penn. Topographical and Geological Survey Bull.*, **M-12**, 268 (1928).
188. Skarzynski, B., and Czekalowski, J. W., *Nature*, **158**, 304-5 (1946).
189. Slater, J., *The Surveyor*, **81**, 199 (1932).
190. Sleeper, B. P., and Stanier, R. Y., *J. Bact.*, **59**, 117-27 (1950)
191. Southgate, B. A., Pentelon, F. T. K., and Bessindale, R., *Biochem. J.*, **26**, 273-84 (1932).
192. Southgate, B. A., *Gas World*, **98**, *Coking Section 14* (1933).
193. *Ibid.*, *J. Inst. Sanit. Engrs.*, **48**, 83-98, 99-114 (1949).
194. Sperr, F. W., Jr., U.S. Patent 1,523,845 (1925).
195. ———, *Am. J. Pub. Health*, **19**, 901-7 (1929).
196. ———, *Am. Gas Assoc. Proc.*, **3**, 282-5 (1921).
197. ———, *Gas Age-Record*, **58**, 73-6, 80 (1926).
198. Stanier, R. Y., Sleeper, B. P., Tsuchida, M., and MacDonald, D. L., *J. Bact.*, **59**, 137-151 (1950).
199. Stevenson, W. L., *Gas World*, *Coking Section*, **21** (1921).
200. ———, *Mining Congr. J.*, **12**, 423-6 (1926); *J. Penn. Water Works Operators Assoc.* (1922).
201. ———, *Am. J. Pub. Health*, **19**, 817-8 (1929).
202. Stokes, H. N., *Econ. Geol.*, **2**, 14-23 (1907).
203. Stone, C. H., *Proc. Am. Gas Assoc.*, **1923**, 1159-1161.

204. Streeter, H. W., *Am. J. Pub. Health*, 19, 929-31 (1929).
205. ———, *Pub. Health Repts.* 44, No. 36, 2149-56 (Sept. 6, 1929).
206. ———, *Ind. Eng. Chem.*, 22, 1343-6 (1930).
- 206a. Streeter, H. W., and Phelps, E. B., *Pub. Health Bull. No. 146* (1925).
207. Temple, K. L., and Colmer, A. R., *Proc. Sixth Ind. Waste Conf.*, 1951, 285-91, Purdue Univ.
208. ———, ———, *Bact. Proc.*, 1951, Abst. of Papers, p. 140.
209. Temple, K. L., Colmer, A. R., and Koehler, W. A., Paper presented at Annual Meeting, Am. Inst. Min. Met. Eng., St. Louis, Mo. (Feb. 19-22, 1951).
210. Tesi, A. F., *Bull. Univ. Pittsburgh*, 40, 303-10 (1944).
211. Theriault, E. J., *Ind. Eng. Chem.*, 21, 343-6 (1929).
212. Thompson, J. I., U.S. Patent 1,402,194 (Jan. 3, 1922).
213. Thornton, E. J., *Inst. Petroleum Tech.*, 19, 957-70 (1933).
214. Tiddy, W., U.S. Patents 2,511,306 (1950); 2,511,307 (1950); *Official Gaz.*, 635, 517 (1950).
215. Tisdale, E. S., *J. Am. Water Works Assoc.*, 18, 574-86 (1927); 23, 1357-65 (1931).
216. ———, *Am. J. Pub. Health*, 19, 820-1 (1929).
217. Tisdale, E. S., and Lyon, E. W., *J. Am. Water Works Assoc.*, 27, 1186-98 (1935).
218. Todd, A. R., *W. Va. Univ. Eng. Expt. Sta. Tech. Bull.*, 11, 18-20 (1938).
219. Tracy, L. D., *Min. & Met.*, No. 161, 29-30 (May 1920); *Trans. Am. Inst. Min. Met. Engrs.*, 66, 609-23 (1922).
220. Travers, J. T., U.S. Patents 1,685,300; 1,685,301 (1928).
221. Trax, E. C., *W. Va. Univ. Eng. Expt. Sta. Tech. Bull.*, 6, 5-19 (1933).
222. ———, *Eng. News*, 64, 362-3 (1910); *Eng. Record*, 62, 371-2 (1910).
223. Tupholme, C. H. S., *Ind. Eng. Chem.*, 25, 303-4 (1933).
224. U.S. Bur. of Mines, Tech. Paper No. 405,343 (1928).
225. ———, *Mineral Yearbook* (1949).
- 225a. *Minerals Yearbook* (1948).
226. U.S. Pub. Health Service, *Manual of Policy Organization and Uniform Practice*, (1936).
227. U.S. War Dept. Report, *Mining Congr. J.*, 12, 523-4 (1926).
228. Waksman, S. A., and Joffe, J. S., *J. Bact.*, 7, 239-56 (1922).
229. Waring, F. H., *Am. J. Pub. Health*, 19, 758-70 (1929).
230. Wells, J. H., and Wilson, P. J., Jr., U.S. Patent 2,132,592 (1938).
231. Wiegmann, H., and Rohl, O., German Patents 706,172 (1941); 734,566 (1943).
232. Wilson, P. J., *Am. Gas Assoc. Proc.*, 11, 934-6 (1929).
233. Winchell, A. N., *Economic Geology*, 2, 290 (1907).
234. Wisner, C. B., U.S. Patents 1,748,815 (1930); 1,756,896 (1930); 1,835,128 (1931).
235. Yancey, H. F., and Fraser, T., *Univ. Ill. Eng. Expt. Sta. Bull.*, 125, 92 pp. (1921).
236. ———, ———, *U.S. Bur. Mines Bull.*, 300, 259 pp. (1929).
237. Young, C. M., *J. Am. Water Works Assoc.*, 8, 201-17 (1921).

General References:

- G-1. Eavenson, H. N., "The First Century and Quarter of the American Coal Industry" (1942).
- G-2. Eldridge, E. F., "Industrial Waste Treatment Practice," New York, McGraw-Hill Book Co., Inc., 300-315 (1942).
- G-3. Ellis, M. M., Westfall, B. A., Ellis, M. D., Research Rept. No. 9, Fish and Wildlife Serv., U.S. Govt. Printing Office, 100-109 (1948).

- G-4. Frost, W. H., Theriault, E. J., Streeter, H. W., and Hoskins, J. K., *U.S. Pub. Health Service Bull.*, **143**, 343 pp. (1926).
- G-5. Fulweiler, W. H., "Rogers Manual of Industrial Chemistry" (C. C. Furnas, Ed.), Vol. I, pp. 578-647, New York, D. Van Nostrand Co., Inc. (1942).
- G-6. "Gas Chemists' Handbook," American Gas Assoc., N. Y. (1929).
- G-7. Gluud, W., and Jacobson, D. L., "International Handbook of the By-Product Coke Industry," New York, Reinhold Publ. Corp. (1932).
- G-8. Hudson Coal Co., "The Story of Anthracite" (1932).
- G-9. Key, A., "Gas Works Effluents and Ammonia," London, Institution of Gas Engineers (1938).
- G-10. Klassen, C. W., Hasfurther, W. A., and Young, M. K., *Proc. Fourth Ind. Waste Conf.*, Purdue Univ., 229-37 (1949).
- G-11. Lowry, H. H., ed., "Chemistry of Coal Utilization," New York, John Wiley & Sons, Inc. (2 vols.), 1945.
- G-12. Mitchell, D. R., ed., "Coal Preparation," 2nd Ed., New York, Amer. Inst. Min. & Met. Engrs. (1950).
- G-13. Moore, E. S., "Coal," New York, John Wiley & Sons, Inc. (1922).
- G-14. Murdock, Harold R., *Ind. Eng. Chem.*, **43**, No. 6, 99a (1951).
- G-15. Niles, Arthur H., *Water & Sewage Works*, **97**, No. 2, 50 (1950).
- G-16. Phelps, E. B., "Stream Sanitation," 267 pp., John Wiley & Sons, Inc., New York, (1944).
- G-17. Scott, W. W., "Standard Methods of Chemical Analysis," 4th Ed., New York, D. Van Nostrand Co., Inc. (1927).
- G-18. Siebert, C. L., *Iron and Steel Engr.*, **23**, No. 7, 78-83 (1946).
- G-19. Southgate, B. A., "Treatment and Disposal of Industrial Waste Waters," pp 105-131, London, His Majesty's Stationary Office (1948).
- G-20. "Standard Method for the Examination of Water and Sewage," 9th Ed. A. P. H. A. (1946).
- G-21. Symons, G. E., *Sewage Works J.*, **17**, 558-72 (1945).
- G-22. U.S. Army Engrs. "The Ohio River," 5th Ed. 1935).
- G-23. United States Steel, "The Making, Shaping, and Treating of Steel" (1948).
- G-24. Whipple, G. C., "The Microscopy of Drinking Water," 3rd Ed., 186-205, New York, John Wiley & Sons, Inc. (1914).
- G-25. Wilson, P. J., Jr., and Wells, J. H., "Coal, Coke and Coal Chemicals," New York, McGraw-Hill Book Co. (1950).
- G-26. Zimmerman, E. W., "World Resources and Industries," New York, Harper & Brothers (1951).

15. Waste Disposal Problems of The Petroleum Industry

Roy F. Weston

Sanitary Engineer in Charge

Robert G. Merman

Senior Chemical Engineer

Joseph G. DeMann

Process Foreman

Waste Control

*The Atlantic Refining Company
Philadelphia, Pa.*

Introduction

For convenience of discussion, wastes related to the petroleum industry have been grouped according to the following activities:

(1) Crude oil producing and handling, including the removal of crude oil from the ground to tankage.

(2) Refining.

(3) Transportation and marketing, including the movement of crude oil from oil field tankage to the refinery, the movement of refined products to distribution terminals and sales stations, and the operation of sales stations.

Crude Oil Producing and Handling

Wastes resulting from the production and handling of crude oil, include drilling muds, oil field brines, free and emulsified oil and tank bottom sludge.

Drilling mud or fluid is used to seal sub-surface pressures, to lubricate and cool the drill and to remove drill cuttings without interfering with the drilling operation. Drilling muds, in recent years, are costly, specially prepared fluids of controlled density, viscosity, surface tension and water-retention capacity. Many different chemicals may be used in the preparation of a mud of the desired characteristics.¹ Some of these materials are barytes, amorphous silica, iron oxide, strontium sulfate, complex phos-

phates and sodium silicate. Caustic soda, soda ash, tanin in the form of quebracho or other bark extract, gallic acid, humic acid, etc., are often used together.

In general, drilling muds are carefully conserved because of the high cost of their preparation. They are continuously treated to condition them for use and are recirculated to prevent loss. As a result, there is little loss of mud at ground level and at the close of drilling the mud is disposed of in the slush pit used during the drilling operation.

The disposal of oil field brines constitutes the principal pollution abatement problem associated with crude oil producing and handling.

Relatively small quantities of salt water may also be obtained from demulsification and desalting processes. In general, these wastes will have the same characteristics as the oil field brines, although, in some cases water-soluble chemicals used in treating the emulsions also will be present.

The quantity of brine produced ranges from about 4 to 96 per cent of the total volume of oil and water produced by the well. The chemical composition of the brines varies considerably with the location of the field and the producing formation. A few typical analyses of oil field brines are shown in Table 1.¹ It is apparent from the analyses in Table 1 that oil field brines contain commercially valuable material. It has been estimated that the Mid-Continent and Gulf Coast fields alone produce 10,000,000 barrels of salt water daily which could provide 4.5 times the annual consumption of crude and refined chloride salts in the United States.² Although the total quantity is enormous, the production available at any one point is usually limited as to volume or uncertain as to the future and could not be expected to compete favorably with existing mining and subsurface dissolving operations of rich salt deposits.

Magnesium is recovered from oil field brines as the hydroxide by precipitation with lime followed by concentration and vacuum filtration.³ Bromine has been recovered but current practice is to use sea water, a more abundant and dependable source.^{3,4} Iodine has also been recovered from oil field brines but today most of the iodine used in the United States is produced as a by-product by the Chilean nitrate industry.² At present, there seems to be no favorable opportunity for the economical recovery of iodine from oil field brines.

Various methods have been used to dispose of oil field brines; solar evaporation of impounded brine, controlled diversion of brine into surface waters and injection of the brine into subterranean formations. While inherently costly, the salt water injection method is currently recognized as the most effective method of disposal with the possible exception of some coastal fields where ocean disposal of the brine is feasible. The injection of brine into the subterranean formation from which it

TABLE 1. TYPICAL ANALYSES OF OIL FIELD BRINES

Field Producing Formation	Specific Gravity at 15.6°C	Total Solids (ppm)	Calcium Ca (ppm)	Magnesium MG (ppm)	Sodium and Potassium Na and K (ppm)	Iron (ppm)	Bicarbonate HCO ₃ (ppm)	Sulfate SO ₄ (ppm)	Chloride Cl (ppm)	Bromide Br (ppm)	Iodide (ppm)	Total Hardness	Alkalinity (ppm)	pH	Reducing Compounds as H ₂ S (ppm)
Illinois:															
Bartlesville-Carlyle	1.032	43,630	861	482	15,424	11	196	8	26,590	52	6	...	126	7.1	2.0
Centralia-Weiler	1.071	98,171	3,330	1,457	32,667	28	106	7	60,440	132	4	...	102	7.2	3.0
Louden-Stray	1.080	113,150	3,680	1,363	38,306	33	194	129	69,379	64	2	...	134	7.7	3.7
Salen-Benoist	1.085	120,858	4,240	1,575	40,381	58	128	90	71,263	120	3	...	47	7.2	3.4
North Aden-McClosky	1.093	131,090	4,769	2,992	41,592	...	143	948	80,450	188	8	...	159	7.7	79.0
Sandoval-Devonian	1.063	87,140	3,860	1,335	27,927	...	301	44	53,530	140	3	...	273	7.0	6.5
Kansas:															
Welch-Chat	...	163,050	7,832	1,985	44,610	...	20	27	88,230	383	...	27,700	107-182*
Silica-Siliceous limestone	...	23,890	1,018	374	6,840	...	666	1,292	12,100	27	...	4,077
Brexford-Kansas City	...	168,950	8,980	3,750	40,070	...	104	56	88,300	458	...	37,817
Cunningham-Lancing	...	251,200	13,188	8,960	57,340	...	39	51	137,500	688	...	69,729
Ritz-Canton-Viola lime	1.031	52,640	4,420	2,230	9,325	...	156	10	28,600	20,193
Oklahoma:															
Sample 1*	1.162	235,982	10,753	2,691	76,915	...	31	348	145,241
Sample 2*	1.081	115,609	5,530	1,625	36,914	...	177	2	71,361
Sample 3*	1.076	107,235	4,708	1,939	34,058	44	66,486
Sample 4*	1.162	238,045	12,822	2,748	75,400	...	92	181	146,804
Sample 5*	1.026	36,167	1,254	396	12,229	...	119	8	22,161
Texas:															
Upton County*	1.007	8,522	822	278	1,611	...	677	2,675	2,429
Kilgore*	...	67,649	1,388	282	21,540	...	569	278	40,598
Longview*	...	68,964	1,432	335	24,653	...	387	259	40,598
Upshur*	...	69,592	1,452	350	25,185	...	250	110	42,245

*H₂S Concentration from 3 fields in siliceous formation are in this range.

NOTE: Barium, Selenium, rare metals and other elements not noted above may exist in brines.

Source of Information:

1. Study of Brine-Disposal Systems in Illinois Oil Fields, Sam S. Taylor, W. C. Holliman and C. J. Wilhelm, U. S. Bureau of Mines, Report of Investigations, R. I. 3534, August 1940.
2. Disposal of Oil-field Brines in the Arkansas River Drainage Area in Western Kansas, C. J. Wilhelm, H. M. Thorne and M. F. Pryor, U. S. Bureau of Mines, Report of Investigations, R. I. 3318, October 1936.
3. Preliminary Report on the Disposal of Oil-field Brines in the Ritz-Canton Oil Field, McPherson County, Kansas, C. J. Wilhelm and Ludwig Schmidt, U. S. Bureau of Mines, Report of Investigations, R. I. 3297, December 1935.
4. The Disposal of Oil Field Brines, Ludwig Schmidt and John M. Devine, U. S. Bureau of Mines, Report of Investigations, Serial 2945, June 1929.
5. Water Analysis of East Texas, *The Oil and Gas Journal*, p. 57, December 1, 1938.

came has the additional advantage of restoring pressure and thereby increasing oil recovery from the formation by about 10 per cent. In Texas, a group of about 250 operators have formed a salt water disposal company to handle their brine disposal problems by injection.⁵ The State Railroad Commission in turn has cooperated with the operators by allowing the extraction of an additional barrel of oil for every 50 barrels of brine returned to the formation. The formation of salt water disposal companies, as a cooperative effort on the part of several producers operating within a given field, is now common practice wherever the volume of salt water produced is sufficient to constitute a pollution hazard.

Satisfactory brine injection, whether for the purpose of disposal alone or of disposal and repressuring, requires brine conditioning. The returned liquid must be chemically stable and free of suspended solids to prevent equipment corrosion and plugging of the sand. In some cases, the brine is kept out of contact with air to prevent the precipitation of insoluble mineral salts resulting from oxidation. In other cases, the brines are purposely aerated to precipitate these materials which are removed by sedimentation and to remove hydrogen sulfide and carbon dioxide. Lime and a coagulant are usually employed following aeration to assist in coagulation and stabilization of the water. It is often necessary to provide chlorination treatment of salt water to be injected in order to control troublesome bacterial growths.

There are several installations employing the dissolved air flotation process for treating California oil field brines prior to discharge into surface waters.⁶ Alum, ferric salts and frequently activated silica are used as coagulants. Effluents contain less than 10 ppm oil and less than 100 ppm suspended solids. The ability of the brine to form hydrogen sulfide as a result of biological action is reduced as much as 90 per cent by this process. The BOD of the brine is also appreciably reduced. The process⁶ is discussed in more detail in the section on Refining.

Oil pollution from crude oil production and handling has been minimized in recent years by the installation of equipment designed to intercept leaks and spills and by over-all good housekeeping practice. The larger and better regulated fields are remarkably free of oil leaks and spills because of careful operation. Oil field emulsions are now satisfactorily broken by mechanical, thermal, chemical or electrical methods so they are no longer a major source of oil pollution.¹

Tank bottom sludges are usually pumped to a burn pit or may be used for road oiling.

Refining

A schematic diagram, Figure 1, shows basic refining operations and the general character of their wastes. The diagram includes operations typical

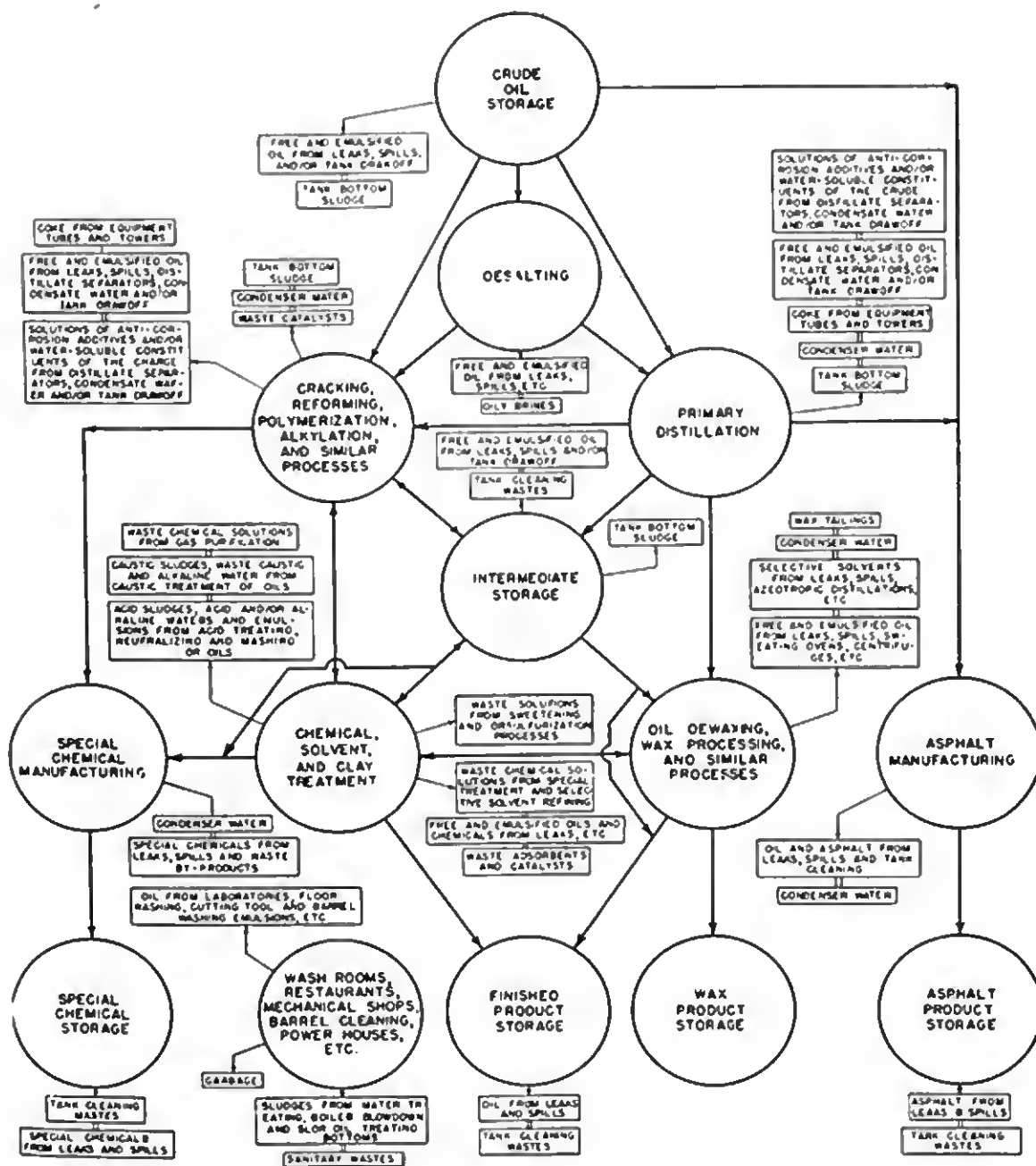


FIGURE 1. Typical wastes produced in petroleum refining

of a complete refinery, i.e., a refinery manufacturing motor fuels, burning oils, lubricating oils and greases, waxes, asphalts and specialty products. It is apparent that a multiplicity of wastes may be produced at a complete refinery. Such wastes may be generally classified as follows:

- | | |
|----------------------|-------------------------|
| 1. Free oil | 7. Special chemicals |
| 2. Emulsified oil | 8. Waste gases |
| 3. Condensate waters | 9. Sludges and solids |
| 4. Acid wastes | 10. Clean cooling water |
| 5. Waste caustics | 11. Sanitary wastes |
| 6. Alkaline waters | |

The various materials that may cause water pollution generally originate in small quantities from a large number of sources widely distributed about the refinery. The sources and characteristics of the various types of wastes are described below:

Free Oil. Large complete refineries may be expected to have the equivalent of 0.1 to 2 per cent of their crude oil charge escape to the sewers in the form of free oil. In the large refinery this oil originates in small quantities from hundreds of individual sampling taps, pump gland leaks, valve and pipeline leaks, losses and spills at times of unit shutdown and equipment repair, accidental spills and overflows, tank bottom draw-offs and other miscellaneous sources.

The characteristics of the oil reaching the sewers vary appreciably from area to area within the refinery depending on the local processing operations. However, the composite from the refinery will approach the characteristics of weathered crude oil. The initial boiling point may be as low as 100°F.

The presence of light ends creates a potential explosion hazard in the sewers. For this reason precautions must be taken in the design of the sewerage system to adequately trap all sewer inlets. Proper trapping of all inlets makes it possible to maintain rich mixtures in many sewers at all times and reduces to a minimum the possibilities of creating explosive mixtures. In addition, proper trapping reduces the possibilities of the spread of fire from one area to another.

Oil exists in the waste water in two fractions. One fraction is carried in suspension in the form of small droplets, small suspended solids-oil agglomerates or oil in water emulsion. The other fraction floats on the surface of the water, usually, as a water in oil emulsion, and is commonly called free oil. The relative concentration of free or floating oil to total oil will vary appreciably. The presence or absence of oil in water emulsions is the largest single variable. Small concentrations of emulsions exist in most waste waters containing oil although emulsion itself is not drained to the sewers. Typical data on the relative concentrations of suspended

and floating oil for waste waters receiving only nominal quantities of emulsion from incidental sources are shown in Table 2.⁷

TABLE 2. DISTRIBUTION OF FLOATING AND SUSPENDED OIL IN WASTE WATER RECEIVING NOMINAL QUANTITIES OF EMULSION

Floating Oil (ppm)	4	12	8	10	5	9	16	3	19	4	8	15
Suspended Oil (ppm)	4	3	5	5	7	5	5	5	5	2	9	7

In practically all cases gravity differential oil-water separators are provided to recover floating oil and to treat the waste. In the process of separating oil from water, oil rises to the surface, sediment settles to the bottom and relatively small concentrations of oil and suspended solids pass through the separator. Some solid matter rises to the surface with the oil and some oil settles to the bottom with the solids. Typical data⁸ on the characteristics of separator skimmings (slop oil) are shown in Table 3, columns 1, 2 and 3, and data on typical separator bottoms (sludge) are shown in Table 2, columns 4, 5 and 6.

The separator skimmings are unfit for return to process units because of their solids and water content. It is generally considered that combined bottom sediment (suspended solids) and water contents in excess of about 1.0 per cent may interfere with efficient processing, may create accident hazards or may shorten "on stream" running time. Therefore, slop oil treatment is necessary to reduce the solids and water content to 1.0 per cent or less. In most cases these emulsions are rather easily resolved by heating to 190°F, retaining at this temperature for 4 to 6 hours and then settling for 12 to 24 hours. At the end of the settling period three definite layers of material will exist. The top layer will be clean oil, the middle layer will be secondary emulsion and the bottom layer will be water containing soluble components, suspended solids and oil. A small amount of material may settle out as an oily sludge. In some cases it is advantageous or necessary to use caustic (sodium hydroxide) or emulsion breaking organic chemicals for resolving slop oil emulsions. Ordinarily, only enough caustic is necessary to adjust the pH of the slop oil to approximately 8.0. The resolution of slop oils having pH values 6.5 to 7.5 appear to be the most difficult. Both lower and higher pH values give better results. The addition of 2 to 15 barrels of waste caustic per 1,000 barrels of slop oil in conjunction with heat treatment has aided in resolving some slop oil emulsions. The characteristics of the water layer⁸ when using waste caustic and heat are shown in Table 4, column 1. In such cases the treatment and disposal of this material present a definite problem. Pilot plant experience using an 0.5 square foot Oliver precoat continuous vacuum filter shows that slop oil emulsions may be successfully resolved by filtra-

TABLE 3. CHARACTERISTICS OF SLOP OILS AND SLUDGES

Column No.	1	2	3	4	5	6	7	8	9
Type Waste	Slop Oil	Slop Oil	Slop Oil	Separator Bottoms Naptha Treating	Separator Bottoms Naptha Treating, Distillation and Tankage	Separator Bottoms Cracking, Alkylation and Polymerization	Secondary Emulsions Slop Oil Treating	Flocculation Sludge Pilot Plant	Slop Oil Bottoms Treating
Source Waste	Naptha Treating	Naptha Treating, Distillation and Tankage	Cracking, Alkylation and Polymerization	Separator A	Separator B	Separator C			
Type Unit	Separator A	Separator B	Separator C	Separator A	Separator B	Separator C	Spent Caustic and Heat-- Plant Scale	Coagulation and Sedimentation	Heat and Caustic
Quantity							17% of Charge	1500#/MG. (Dry)	33#/Bbl. Oil Recovered
Spec. Grav.	0.746-0.767	0.766-0.828	0.856-0.901	1-1.06	1.0-1.01	1.02-1.08			0.93
% Oil Wt.	64.5	49.9	71.6-93.4	4.8-10.5	19.0-20.0	0.29-1.1		1.6	30
% Solids Wt.	0.24	0.5	1.4-6.4	54.0-79.0	74.0-75.0	13.5-18.0	8	3.0	3
% H ₂ O Wt.	35.3	49.6	6.4-13.5	2.4-5.0	80.0-85.0	12	95.4	67
B.T.U./# Dry Solids				5,500-10,800	7,405-7,590	6,213	70	10,000	...

TABLE 4. CHARACTERISTICS OF TYPICAL REFINERY WASTES

Column No.	1	2	3	4	5	6	7	8	9
Type Waste	Water Layer	Water Layer	Milk Water Emulsion	Emulsion	Emulsion	Emulsion	Condensate	Condensate	Condensate
Source of Waste	Slop Oil Treatment	Slop Oil Treatment	Water Wash Bar.	Condenser	Jet Vacuum Pump	Desalting	Low Sulfur Gas Separator	Vis. Breaker Gas Separator
Type Unit	Spent Caustic and Heat—Plant Senle	Vacuum Precoat Filter—Pilot Scale	Treating	Combination Unit	Lube Oil Vacuum Still	Desalting Unit	Combination Unit	Combination Unit	Light Oil Recovery
Quantity of Waste	1 Bbl/Bbl Product
Acidity (ppm)
Alkalinity (ppm)	15,313	59.5	520	739	1,518	2,963	69-13,175
Ammonia (ppm)	4.1	225	2.0	500	130-999	3-8,350
B.O.D. (ppm)	5,660-14,440	77-153	7,900	425	404	408	3,040	55-9,500
C.O.D. (ppm)	22,000-56,000	500-1,360	86,775	72.3	865-3,031	1,204	7,239	214-16,255
Odor Threshold	1.0	1.8	2.5	1.5	3.5
Oil (ppm)	4,900-10,300	37-130	31,600	236	94.3	32-713	3	2.5	6-230
pH	10-10.2	6.9-7.7	9.79	7.22	7.03	9.26	8.5	7.85	5.0-9.2
Phenol (ppm)	2.3	4.1	0.06	156	0-213
Sulfide (ppm)	1.3	600	1,500	T-5,000
Suspended Solids (ppm)	60-940	30-139
*TLM (24 Hr.)	14

* Approximate 24 hour Median Tolerance Limit for Bluegill Sunfish—expressed as per cent concentration of waste.

TABLE 4. CHARACTERISTICS OF TYPICAL REFINERY WASTES—CONTINUED

Column No.	10	11	12	13	14	15	16	17	18	19
Type Waste	Acid	Acid	Spent Caustic	Spent Caustic	Spent Caustic	Carbolate	Alkaline	Special Chemicals	Special Chemicals	Refinery
Source of Waste	Unit Sewer	Unit Sewer	Alkylate Wash	Naphtha Wash	Naphtha Wash	Naphtha Wash	Shut-down	Unit Sewer	Unit Sewer	Separator
Type Unit	Alkylation Unit	H ₂ SO ₄ Sludge Conversion Unit	Chemical Mfg.	Catalytic Polymerization	Treating	Fluid Catalytic Cracking Unit	Caustic Methanol Sweetening	Alkylation Sulfonation	Detergent Drying	Islet
Quantity of Waste	0.21# NaOH used per # product	0.8% NaOH used per bbl. product	9.6 mgd.
Acidity (ppm)	1.105-12.325	1,140-10,050	18-245	0-188
Alkalinity (ppm)	46,250	209,330	80,020	247,900	150	0-92
Ammonia (ppm)	1.2	2-13	1.8	0.2-12.6
B.O.D. (ppm)	31	10-272	256	8,440	51,154	363,600	28-151	8-1,180	96-501
C.O.D. (ppm)	1,251	910	3,230	50,350	144,120	901,200	371-299,000	250-5,382	2,585-51,350
Odor Threshold	3.7	3-5	1.5	1.2	3.25-5.32
Oil (ppm)	131.5	124	10	T-12	8-58	13-1,310	40-7,750	3,900-6,500
pH	0.6-1.9	1.71	12.8	12.9	13.4	13+	9.5-12.5	4.6	7.37-9.31	2.4-6.2
Phenol (ppm)	50	22.2	23,312	309,300	0-7.4	0.5-7.9
Sulfide (ppm)	2	3,060	0-3,380
Suspended Solids (ppm)	253	54-279	678	131-678
*TLM (24 Hr.)	0.4	3	0.04	33

*Approximate 24 hour Median Tolerance Limit for Bluegill Suafish—expressed as per cent concentration of waste.

**Waste represents combined discharges from a complete refinery with the exception of naphtha treating wastes.

tion through diatomaceous earth.⁸ Filtration rates of 2.3 to 6.8 gallons per square foot per hour (the range in numerical values shown includes the central 50 per cent of the data) were obtained when filtering at about 170°F. The solids removed by filtration varied from 0.043 to 0.182 pounds per square foot per hour. The cake obtained averaged about 21 per cent moisture and 28 per cent oil. The fuel value of the cake was 12,700 btu per pound. The water layer separating from the clean oil has characteristics as shown in Table 4, column 2. It should be noted that the pollution load is much less than that from caustic and heat treatment. The fact that filtration will resolve slop oil emulsions indicates that the suspended solids present are probably the stabilizing agents.

Typical data on the characteristics of slop oil treatment secondary emulsions⁹ are shown in Table 3, column 7. The quantity of these emulsions ordinarily averages about 17 per cent of the charge. The volume is excessively large at localities troubled with biological growths in the sewerage system or separation facilities. These secondary emulsions can be reduced in volume by about 55 to 60 per cent by treatment with organic emulsion breaking compounds.

Gravity differential oil-water separators cannot remove oil in the form of oil in water emulsions or in the form of oil-suspended solids agglomerates with specific gravities approximately that of the water. An estimate can be obtained of the probable oil content of gravity-differential separator effluents by determining the susceptibility to separation (STS) number of the waste.⁸ The numerical value of the number is representative of that concentration of oil that cannot be separated by normal gravity differential means. Typical susceptibility to separation data for various separator influents are shown in Table 5.

Emulsions. The presence of oil that cannot be separated from waste waters by conventional gravity differential means is of considerable economic importance to the refiner because of the loss of valuable product and the need for costly facilities to treat the effluent from his oil recovery separators.

An oil in water emulsion has turbidity as its chief characteristic and usually has a milky or pearly-gray appearance. This type of emulsion is not removed in the gravity type oil separator, and when it is discharged into a large stream or body of water, it usually breaks as a result of dilution and the oil rises to the surface of the water.

Emulsions may be formed in the sewerage system as a result of intimate contact between oil, water, and emulsifying agents or may originate directly as process by-products.

The occurrence of coke, clay, sanitary sewage, water treating plant sludges and other flocculent and fibrous solids appears to increase the con-

centration of nonseparable oil. The presence of tars, asphalts, petroleum sludges, soaps and numerous solvent and treating chemicals also increases the nonseparable oil content of waste waters. The pumping of waste water is especially conducive to the formation of emulsions as shown by the susceptibility to separation values for separators C and E, Table 5.

TABLE 5. SEPARATOR OPERATION DATA

Separator	Flow (ingd)	Overflow Rate (ft/min.)	Specific Gravity Oil	Oil Content (ppm)			% Reduction Separable Oil
				Influent	S.T.S.	Effluent	
A	4.8-5.9	.027-.033	.746-.767	40-150	5-21	14-47	65-92
B	3.2-3.9	.047-.057	.766-.828	39-63	7-15	12-37	40-80
C	7.2-8.6	.025-.029	.856-.901	37-70	14-24	21-41	39-79
D-1	4.2-4.8	.140-.158	0.93	50-97	16-38	26-52	60-98
D-2	4.2-4.5	.137-.149	0.93	50-107	18-39	21-40	76-100
E	0.144	.433	.856-.901	235-510	47-83	105-210	57-83
E	0.072	.217	.856-.901	220-350	60-106	108-163	57-83

Ranges shown include the central 50% of the data.

S.T.S. is the susceptibility to separation number.

Separators A, B and C are of ancient design, made up of a series of relatively small compartments.

Separator D-1 is a conventional 2-stage A.P.I. design.

Separator D-2 same as D-1 with second stage inlet device replaced with streamlined vertical guide vanes.

Separator E is an experimental single stage A.P.I. design.

Influent to Separator E was pumped from the influent to Separator C by a centrifugal pump through about 400' of 3" pipe.

The direct formation of emulsions may result from the chemical treatment of lubricating oils, waxes and burning oils, from distillate separators, from barometric condensers, tank drawoffs, desalting operations, pump gland leakage, special chemical manufacturing, acid sludge recovery processing, wax deoiling, barrel and truck washing, machine shops and other sources. Data illustrating the characteristics of some of these wastes are shown in Table 4, columns 3 to 6 inclusive.

Emulsions formed in the water washing of acid treated lubricating and wax stocks following neutralization are generally known as "white water" or "milk water." These emulsions are very stable. Samples stored at room temperatures have remained stable for several years. They contain 1 to 3 per cent oil by weight. Batch treatment processes will produce about one barrel of milk water per barrel of product. In some cases it is possible to prevent the occurrence of these or similar types of emulsions by the use of special chemicals or special operating techniques. At one Schutte wax deoiling plant and at one barrel washing plant the formation of emulsions

was prevented by the use of calcium chloride in the recirculated process water. The cost of breaking treating plant emulsions using calcium chloride is about 1.5 to 2 cents per barrel at one refinery.

Sulfonic acids and resinous materials may be recovered from some of these emulsions but generally they can be used only as fuel.¹⁰ This is true because the heterogeneous nature of the recovered material necessitates refining procedures equivalent to those required for the manufacture of similar products of better quality from more reliable sources of raw material.

One refinery utilizes another waste material to treat water-soluble petroleum sulfonates produced in the manufacture of white oils.¹¹ The sulfonate waste is acidified to a pH of 5 with acidic waste water from a sulfuric acid sludge conversion plant. The sulfonic acids formed are precipitated with hydrated lime at a pH of 7 to 8.4. Reductions of 98 and 93 per cent are obtained in color and oxygen consumed, respectively. The scum and sludge are pumped to a lagoon.

The quantity of emulsions resulting from barometric condensers and jet vacuum pumps has been successfully reduced by the use of a "dirty water" cooling tower system in a number of cases. In other cases, surface condensers have been substituted for barometric condensers and have been provided on jet vacuum pumps to prevent the formation of this type of emulsion.

Various chemical processes are in use to treat emulsions which must be discharged from the units. In some cases these processes are applied locally to the discharges of individual units, while in other cases they are used on the effluent of plant separators. One refinery presently treats emulsion resulting from steam vacuum jets on crude distillation units with caustic.¹² Oil is the continuous phase in this emulsion which contains about 50 per cent water. Naphthenic acids and probably naphthenic soaps are the emulsifying agents. Approximately 150 to 250 pounds of sodium hydroxide are used per 1,000 barrels of emulsion. Although some fresh caustic is used, laboratory studies have shown that spent caustics from the neutralization of hydrogen sulfides, sulfur dioxide and/or sulfonic acids could be used satisfactorily for this purpose if they contain sufficient alkalinity. The process involves mixing the caustic with the emulsion, heating and settling. The water-caustic solution from the process is drawn to the sewer.

A Canadian refinery currently treats a segregated waste water flow containing emulsions by the conventional coagulation and sedimentation process.¹³ The treatment plant handles one million gallons per day and consists of a 40-foot diameter oil flotation tank for removing free oil, a building for pumps, chemical storage and chemical feeding equipment, a

flash mixer and flocculation tank, a 60-foot diameter settling tank and glass covered sludge drying beds. The oil content of the waste as it leaves the flotation tank is 175 ppm and less than 5 ppm as it leaves the settling tank.¹³ Approximately 3 grains per gallon of hydrated lime and commercial ferrous sulfate are required to accomplish this removal. The glass covered sludge drying beds were abandoned shortly after the plant was placed in operation in favor of sludge lagoons.

The application to petroleum wastes of the conventional coagulation and sedimentation process as it has been used in the treatment of domestic water supplies, has presented several problems, chiefly in connection with the settling of the floc. The presence of oil in the floc contributes considerable buoyancy to the particles, thus adversely affecting their settling characteristics. As a result, settling tanks must be constructed with larger surface area to settle these light flocs. An overflow rate of 800 to 1,000 gallons per day per square foot of surface area is common in the domestic water treating field. The settling tank at the Canadian refinery previously mentioned has an overflow rate of 355 gal/day/sq ft. The necessity for a low rate of this magnitude has been substantiated by independent work conducted by the authors.¹⁷ This work included pilot plant studies of the conventional coagulation and sedimentation process and the sludge recirculation principle as provided in a package type unit. The effect of activated silica and ground clay as coagulation aids was also investigated. From these studies it was concluded that chemical coagulation was entirely practical for the treatment of petroleum wastes and that removals of 90 per cent, 80 per cent, and 70 per cent, could be expected for oil, suspended solids and BOD respectively. The use of either activated silica or clay made it possible to double the throughput capacity without loss in efficiency. The study indicated that the sludge recycle type of unit can be designed for about twice the overflow rate as the conventional sedimentation units for equivalent efficiencies. On the basis of these results, a treatment plant was designed and is now under construction to handle a normal flow of 9.6 mgd of refinery wastes (see Figure 2). This plant will include two 100-foot diameter Cyclators in which the coagulation and sedimentation process will take place. It is expected that the effluent will average 10 ppm oil, 12 ppm suspended solids and a 70 per cent reduction in BOD.

A midwestern refinery¹⁴ utilizes coagulation and sedimentation processes of the sludge recirculation type, followed by filtration through anthracite filters to condition refinery effluent for reuse and for disposal. Prior to the installation of treatment facilities, the plant discharged on the average 1,500 gpm of water from the cooling water system to a nearby river in which the flow dropped as low as 1,000 gpm during periods

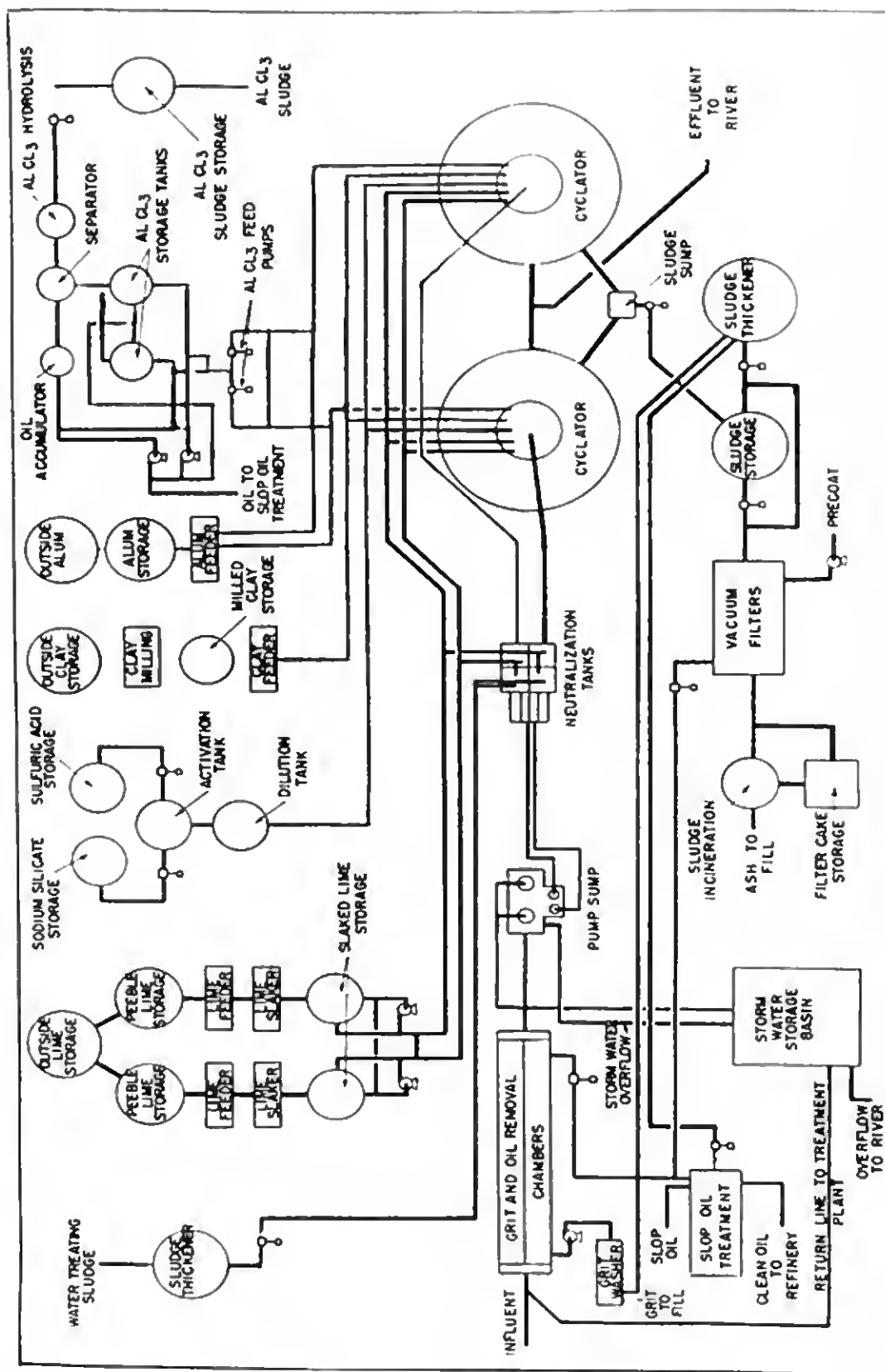


Figure 2. Simplified flow diagram of a chemical flocculation waste treatment plant

of extremely dry weather. The treatment facilities have reduced this flow to 140 gpm and provided a better quality water for cooling tower make-up.

The plant effluent to the river is free of oil and phenol but is amber in color due to dissolved organic matter. The water returned as cooling tower make-up contains 20 ppm oil and 128 ppm total hardness as compared with 250 ppm oil and 357 ppm total hardness in the influent to the main treatment system.

There are numerous modifications of the conventional coagulation and sedimentation process. Perhaps the most unique to this date is one in which the floc is removed by flotation. Success of the separation depends on the release of minute particles of dissolved air which become attached to the floc particles and carry them rapidly to the surface. The advantage of this process is that appreciably smaller surface areas are required for separation. Installations of this type treating California oil field brines are designed for overflow rates on the order of 2.6 gallons per square foot per minute and produce effluents having less than 10 ppm oil and 100 ppm solids.⁶ Other installations include the treatment of emulsified oil from tank car washings near Los Angeles^{6,15} where the oil content is reduced from 1,500 to 10 ppm, and the treatment of soap wastes in Massachusetts.¹⁶ The latter installation is designed for 3 gallons per square foot per minute and removes 96 per cent of the fatty acids and soaps present. The net value of the material recovered is enough to pay operation costs and amortization of capital investment.¹⁶

The removal of emulsified oil and other contaminants from refinery waste waters by means of coagulation and sedimentation processes usually presents another problem, namely, the disposal of the resulting oil laden sludge. On the basis of the authors' pilot plant studies, on the average about 1,500 pounds of dry sludge are produced per million gallons of waste treated. These studies indicated that the sludge obtained from the settling tanks contained about 1 per cent solids but could be concentrated by additional settling or mechanical thickening to about 5 per cent.

In some cases it has been possible to dewater sludges in drying beds or lagoons and dispose of the solids in dumps. However, where land is not available and where local conditions do not permit disposal in this manner, a more elaborate treatment must be provided. The authors have studied several methods,¹⁷ such as vacuum filtration followed by incineration and vacuum thickening followed by spray drying and incineration. It was found that the sludge can be dewatered on a vacuum precoat filter to about 45 per cent water content and incinerated with the production of heat in excess of that required to sustain combustion.

Vacuum thickening studies indicated that these sludges can be thickened to about 10 per cent solids. Spray drying and incineration of the thickened

material on a plant scale test proved satisfactory from an operational standpoint. However, loss of about 40 per cent of the oil in the sludge via the drier stack gas made it necessary to supply auxiliary fuel.

Condensate Waters. Condensate waters, as referred to herein, originate from distillate separators, running tanks and barometric condensers. It has been reported¹⁸ that condensate waters from distillate separators may contain one or more of such compounds as organic and inorganic sulfides, normal or acid sulfites and sulfates, sulfonic acids and their salts, mercaptans, amines, amides, quinalines and pyridines, naphthenic acids, phenols, etc. They may also contain chemicals used for corrosion prevention such as ammonia, caustic soda, calcium hydroxide, etc. Not all these substances will be found in a specific waste water at the same time. Waste of this type may also contain suspended matter such as coke, iron sulfide, silica, metallic oxides, soaps, emulsions, sulfonic and naphthenic acids, insoluble mercaptides and other suspensoids.¹⁸ Typical characteristics of condensate wastes are shown in Table 4, columns 7, 8 and 9.

It has been possible in some instances to reduce the quantity of condensate wastes through the use of "dirty water" cooling tower systems for barometric condensers and jet vacuum pumps. In other cases, surface condensers have been substituted for barometric condensers and provided on jet vacuum pumps to control the quantity and strength of this type of waste. Reduction in the quantity of condensate wastes not only lessens the waste disposal problem but also may reduce the loss of valuable water-soluble material.

In cases where the water-soluble constituent forms a constant boiling mixture with water, it is sometimes possible to reduce losses by azeotropic distillation. In one case, a phase separation on cooling made it possible to reduce solvent losses from condensate waters by the use of two azeotropic distillations, one for the solvent rich layer and one for the water rich layer.

The installation of a stainless steel mat (called demister) in an asphalt stripper at a propane deasphalting unit has prevented the carry over of asphalt in the tower overhead. As a result, spray condenser water which condenses the stripping steam, can be recycled to a cooling tower. Approximately 500 gpm of asphalt contaminated water has been eliminated from the sewer in this manner.²⁴

Refineries that process sour crudes usually produce condensate wastes high in sulfides. These wastes contain large amounts of hydrogen sulfide and ammonium sulfides, probably combined as polysulfides, and possibly some sodium and potassium sulfides. A survey of a large refinery which processes considerable quantities of sour crude oil revealed that the

quantities of sulfide outlined in Table 6 were entering the refinery sewers.¹⁹

TABLE 6. APPROXIMATE SULFIDE CONTENT OF PROCESS WASTES FROM REFINERY OPERATING UNITS

	Flow (BPD)	Sulfide #/D
Crude oil desalter	100	532
Thermal cracking unit gasoline receivers	1,900	746
Crude oil distillation unit gasoline dehydrators	200	119
Catalytic cracking feed flashing unit ejector standpipe water	2,400	218
Potassium phosphate hydrogen sulfide scrubbing unit regenerator	2,600	1,047
Catalytic cracking accumulator and potassium phosphate regenerator waters	2,500	1,000
Total	9,700	3,662

Most of the hydrogen sulfide in these wastes and a high percentage of the ammonia can be successfully removed by steam stripping. A California refinery removes all of the hydrogen sulfide and about 90 per cent of the ammonia from 1,400 B/D of waste water containing 3,600 pounds of hydrogen sulfide and 4,800 pounds of ammonia.²⁰ Stripping is done in a 30-foot column, 4 feet in diameter, containing 12 bubble trays. The operation requires 144,000#/D of 20# steam. The pH of the waste is known to affect the amount of hydrogen sulfide removed and the steam requirements. In some cases, pH control of the stripper feed is used.^{19,21}

Pilot plant investigations have indicated that hydrogen sulfide can be successfully stripped from sulfide-bearing wastes with flue gas.¹⁹ Elevated temperatures, 140 to 170°F, appear to appreciably reduce the quantity of gas required.

Sulfides can also be removed from these wastes by oxidation with air. The sulfur is converted to thiosulfate and/or colloidal sulfur, depending on the degree of oxidation. Elevated temperatures increased the rate of oxidation. Ammonia and some hydrogen sulfide is released. A modification of this process is air stripping in which the aeration is carried out at a lower pH and more sulfide is converted to hydrogen sulfide.

The hydrogen sulfide produced in the treatment of these wastes is usually burned for recovery of the fuel value. Proper combustion equipment and location are important to insure dissipation of the sulfur dioxide produced. In one case, the ammonia is reacted with waste sulfuric acid to produce ammonium sulfate for fertilizer.²⁹

Current studies by the authors indicate the possibility of materially reducing the sulfide content of condensate wastes by using organic corrosion inhibitors and maintaining a lower pH in the tower overhead. Sulfide

contents of 100 to 150 ppm have resulted from pH's of about 6 while for the same crude a pH of 7.4 produced sulfide concentrations over 500 ppm.

Condensate wastes from catalytic cracking units frequently contain appreciable quantities of phenolic material in addition to ammonium polysulfides and usually require different treatment methods than those discussed above. In some instances, advantage is taken of the need for water to control the temperature at the top of the catalyst regenerator and to condition the flue gas entering the Cottrell precipitator. Condensate wastes from the unit are collected and sprayed into the regenerator and the inlet duct of the precipitator.

Pilot plant studies by the authors have indicated that phenolic condensate wastes can be successfully treated using a biological filter. Biochemical oxygen demand and phenol reductions respectively were 75 per cent and 72 per cent. These results were obtained at temperatures between 80 and 95°F for phenol concentrations between 50 and 100 ppm. Hydraulic loading on the filter was 15 mgd and no recycle was employed. Phenol was added to the unit waste to obtain these concentrations. Studies on the effect of recycling indicate that substantial increases in reductions of BOD and phenol can be accomplished by recycling about 4 volumes to 1 volume of forward flow.

In some cases where quantities are small, it is possible to dispose of this material by evaporation in furnace stacks or by spraying directly into a furnace.

Acid Wastes. Sulfuric acid is used extensively in the petroleum industry both as a treating agent and a catalyst. Other acids and acid salts also used as catalysts include hydrofluoric acid, phosphoric acid, aluminum chloride and zinc chloride. Acid bearing wastes originate from the acid treatment of gasoline, white oils, lubricating oils and waxes; from the handling of acid sludges and the recovery or manufacture of acid; from the alkylation of motor fuel stocks; from the use of acidic catalysts; and from special chemical manufacturing. The wastes occur as rinse waters, scrubber discharges, spent catalyst, sludges, condensate waters, and miscellaneous discharges resulting from sampling procedures, leaks and spills and shutdowns. Typical data showing the characteristics of discharges from an alkylation unit and a sulfuric acid sludge conversion unit are shown in Table 4, columns 10 and 11.

Acid wastes from pump gland leakage and sampling may be collected locally and returned to the process. Substantial reductions in loss of acid to the plant sewers have been attained by this procedure.

Petroleum products are treated with sulfuric acid to improve color, odor and stability and to reduce gum content and remove sulfur. Acid requirements and concentrations vary widely with the characteristics of

the hydrocarbon and the objective in treating. In general, acid requirements vary from 0 to 60 pounds per barrel using acid concentrations of 85 to 104 per cent.²² One large complete refinery averages about 2.5 pounds of acid per barrel of crude oil charged. Acid treatment of oils results in the formation of sulfur dioxide and an acid sludge. The sulfur dioxide is generally blown out of the oil to the atmosphere. Where this practice creates an atmospheric pollution problem, the sulfur dioxide may be absorbed in water or alkaline solution and discharged to the sewer or may be collected and recovered for acid manufacture or elemental sulfur production.

The acid sludges produced by the sulfuric acid treatment of oils vary considerably depending on the amount of acid used and the characteristics of the treated stock. The consistency of the sludge may vary from that of a low viscosity fluid to that of a highly viscous material that will solidify on standing. The specific gravity of representative acid sludges may vary from about 1.2 to 1.8 and the sulfuric acid content from about 25 to 80 per cent.

The characteristics and quantity of sludge produced afford utilization opportunities to most refineries. The methods of utilization² are varied and include: burning immediately as fuel; treatment to produce by-products such as oils, tars, asphalts, resins, fatty acids, sulfonic acids, ammonium sulfate, metallic sulfate, coke and other materials; and regeneration for acid recovery. A patent has been issued for the manufacture of a water softening material by the reaction of petroleum acid sludge and the solids of waste cellulose sulfite liquor.

Although some refineries use acid sludges as fuel^{2,19} alone, after fluxing with fuel oil, after neutralization with alkaline sludges or alkali or after some combination of these procedures, the probable need of special facilities to minimize corrosion, the high cost of handling and the atmospheric pollution problem due to sulfur dioxide limit the application of this method.

The sludge formed from the acid treatment of light oils is sometimes neutralized with alkaline wastes and discharged to the plant sewers. This practice is not recommended if other alternates are available.

Utilization of acid sludges to recover sulfuric acid offers the best means of handling the disposal problem at most refineries. It is possible to manufacture 50 per cent or more of a complete refinery's acid requirements from acid sludge.

The processes for the recovery of sulfuric acid are basically either hydrolysis or thermal decomposition processes.²¹ Sulfur is recovered by a modification of the thermal decomposition process.

Upon hydrolysis, sulfuric acid sludges resolve into two phases: a weak

sulfuric acid layer and a tarry acid oil layer. The latter is usually burned as a fuel. About 40 to 65 per cent of the acid used can be recovered by concentrating the weak acid layer. This material is black in color but contains a relatively small amount of carbonaceous matter. The addition of water in the hydrolysis operation is controlled so the acid concentration of the water layer is not less than 40 per cent. A number of different type concentrators have been used for this material. Concentration is generally carried out by direct contacting of the acid with hot gases at atmospheric pressure, or by indirect heat transfer which utilizes steam or a similar heat source in a unit which may be operated under vacuum.

In some cases, the weak acid produced by hydrolysis may be used as a source of acid in waste treatment operations such as breaking emulsions, neutralizing alkaline wastes, etc., or it may be used to dilute stronger acid to the desired strength instead of using water.

In the thermal decomposition process, the sludge is decomposed to sulfur dioxide, water and coke in a continuously operating kiln at temperatures about 500°F. The sulfur dioxide is converted to sulfuric acid by one of the conventional catalytical contact processes or into free elemental sulfur. Experience has been that from 85 to 90 per cent of the sulfur in the sludge can be recovered in this manner.²¹

The sludge conversion-contact acid plant method can produce white acids of 98 to 105 per cent concentration or higher.² Black acids of the same strength can be produced by feeding weak acids obtained by hydrolysis to the towers in the place of clean water. This type of recovery plant has the advantage that clean acid can be produced, if desired, and that auxiliary equipment can be installed for the conversion of hydrogen sulfide to sulfuric acid and facilities can be provided for burning sulfur for acid manufacture. Unfortunately, this type of recovery plant is not in general economically applicable to smaller refineries for production under about 25 tons per day.

The sludge conversion-contact acid plant has its own waste disposal problems. The waste water streams may contain sulfur dioxide, sulfuric acid, coke and oil in water emulsions. In one refinery, a sulfur dioxide bearing waste from a contact cooler in the acid recovery plant is used in the treatment of a petroleum sulfonate waste.¹¹ Sulfur dioxide may also be stripped from waste water and utilized. The coke is usually recovered by sedimentation, dried and burned as fuel. Emulsions may be broken using alum or other materials and the oil recovered as fuel.

Sulfuric acid and hydrofluoric acid waste may originate from the alkylation of feed stocks for the manufacture of aviation gasoline. The sulfuric acid alkylation process produces about 50 barrels of approximately 90 per cent acid per 1,000 barrels of product. In view of threatened short-

ages of sulfuric acid, many refineries are re-using and regenerating spent acid from their alkylation operations.²³ In some cases the spent acid is returned to the acid supplier. Applications in the refinery for re-use include acid treatment of naphthas, furnace oil, lubricating oil and waxes. The acid is recovered from the sludges produced as described in the discussion on the disposal of acid sludges.

Hydrofluoric acid wastes originate in the form of acid tars and the bottoms from the azeotropic distillation of the acid in the regeneration process. The acid tars are usually burned as produced or after leaching with caustic. The constant boiling mix bottoms from the acid regeneration procedure are generally treated with lime to precipitate calcium fluoride which is collected and buried. The presence of the sodium ion reduces the effectiveness of the lime in precipitating the fluoride.

The use of oyster shells in trenches receiving leaks and spills containing fluorides has effectively reduced the quantity of fluoride reaching plant sewers.

Another source of acid in some refineries is the aluminum chloride catalyst used in the production of alkylates for the manufacture of detergents. The aluminum chloride is present in a waste material commonly referred to as a sludge. Actually the material is fluid, having a gravity of 1.1 and containing 32 per cent aluminum chloride, 30 per cent benzol and 38 per cent oil by weight. Due to the highly desiccant nature of the aluminum chloride, this material is difficult to handle. It reacts vigorously with water, releasing hydrochloric acid gas, benzene vapor and forming an oil layer and a water layer containing aluminum chloride. The reaction is exothermic and will produce coke if insufficient water is present. In the anhydrous state it is not corrosive to steel but will absorb moisture from the air and become corrosive. Exposure to atmospheric moisture also causes coking which tends to plug small lines and orifices. At one refinery, aluminum chloride sludge, is hydrolyzed to produce aluminum refinery waste water (see Figure 2). Oil and benzol are recovered as slop chloride solution for use as a coagulant in the chemical treatment of the oil. Aluminum chloride in excess of treatment plant requirements is neutralized with lime. The resulting sludge is disposed of along with other treatment plant sludges.

Phosphoric acid catalyst has been satisfactorily handled by leaching. The spent material is dumped into a leaching box where it is leached at a slow continuous rate by displacing water from the pit to plant sewers. The acid-free Kieselguhr or clay is disposed of as fill.

Waste Caustics. Waste caustics as referred to herein originate from the caustic washing of light oils to remove mercaptans, hydrogen sulfide, and other acidic materials that may occur naturally in crude oil or

any of its fractions or may be produced by a variety of processing methods.

The characteristics of various waste caustics from different sources are shown in Table 4, columns 12, 13 and 14.

The quantity of waste caustic produced will vary greatly depending on the characteristics of the crude and the methods of processing.

The constituents of waste caustics responsible for their potent pollution characteristics include mercaptans, thiophenol, thioeresols, phenols, eresols, disulfides, alkylsulfides, the sodium salts of any one of a number of saturated mono acids, naphthenic acids or sulfonic acids and other materials.²

The satisfactory disposal of waste caustic is a major problem at most refineries. The problem is lessened in some cases by process replacement or improvement to achieve more efficient utilization of available treating capacity. Regenerative systems have been used to eliminate the discharge of spent caustic from mercaptan and hydrogen sulfide removal operations. Likewise, the "down grading" use of spent solutions from one process as a treating agent in another has proven advantageous. For example, discarded solutions from doctor treating, after having been made essentially lead free, may be used as prewashes for other treating operations such as scrubbing of hydrogen sulfide from distillates and gases.²¹

Spent caustics from the treating of motor stock from catalytical cracking processes, commonly called carbolates, have been sold as such for the recovery of phenolic constituents. In some cases, this waste is first acidified to release "acid oils" which are separated from the waste layer and sold for their phenolic content. Acid oils from carbolate solutions are approximately 90 per cent phenolic and amount to about 50 per cent of the volume of the carbolate. Typical characteristics of carbolate solutions are shown in Table 4, column 15.

The low acid oil content and the heterogenous nature of the constituents make spent caustic from doctor treating a poor source of recoverable by-products. Studies at one refinery indicate that the acid oil content of this material is 3 to 10 per cent by volume and is 60 per cent phenolic and 40 per cent naphthenic.

Acid oils may be released or "sprung" from spent caustic solutions by neutralization with mineral acids and acid gases. Frequently waste acidic material such as spent acids and acid sludges from other refinery operations may be used for this purpose. The sulfides are converted to hydrogen sulfide which may be burned or recovered and the acid oils are burned as fuel. The water layer from this reaction is usually drawn to the sewer, preferably at a low rate since it still contains a relatively high concentration of oxygen consuming materials.

Flue gases have been used in some cases for the treatment of waste caustics. The caustic solutions are neutralized by the flue gases at temperatures of 160 to 180°F to about pH 5 to release the acid oils, unoxidized hydrogen sulfide and mercaptans and certain weak organic acids. During this process the easily oxidized mercaptides and sulfides are partially oxidized. The acid oils separated from the solution collected are used for fuel or a source of special chemicals. The hydrogen sulfide and odorous materials released to the gas stream must be conducted to burning facilities for atmospheric pollution control. The remaining water solution contains a mixture of carbonates, bicarbonates, sulfates, sulfites, thiosulfates, phenols, etc., which may require further oxidative treatment prior to discharge to natural waters.

Recently a method for utilizing spent pickling acid from the steel industry for the disposal of spent caustics has been developed.²¹ The sulfides and many of the organic acids are removed by precipitation and filtration, and the remaining organic acids are extracted with naphtha. The final solution is suitable for discharge into the refinery drainage system. The spent pickling acid used in this process contains from 1 to 5 per cent of sulfuric acid and from 20 to 30 per cent of ferrous sulfate.

Waste caustics high in sulfides are treated by contact with steam and air in a packed tower at one refinery.²⁴ The sulfides are converted to thiosulfates. The process operates with approximately 95 per cent conversion.

Spent caustics or the liquors resulting from the neutralization of spent caustics may be treated by biological oxidation. Investigations using table top aeration experiments and small scale biological filter experiments as reported by Weston and DeMann²⁵ and extensive biological treatment experiments reported by Degnan, Merman and DeMann²⁶ and Baker, Degnan and Weston²⁷ all indicate the feasibility of the biological treatment of waste caustics and other refinery wastes.

Filter studies showed that oil concentrations of at least 100 ppm had no effect on BOD removal. Sludge from the filter effluent settling tank contained about 31 per cent oil on an oil free, dry basis. Temperatures of 85 to 90°F appeared to be optimum and recycle ratios of 4 to 5 to 1 materially increased reductions. Sulfide concentrations in excess of 10 ppm were found to have a detrimental effect on BOD reduction.

Pilot plant investigations using the activated sludge process indicate that the presence of oil does not adversely affect the oxidative capacity of the sludge for materials like phenol but does seriously interfere with the settling characteristics of the sludge and thereby reduces general treatment efficiencies.

Alkaline Waters. Alkaline waters, as differentiated from alkaline condensate waters and waste caustics, may originate from the washings of neutralized acid treated oils, the washings of caustic treated oils, the dehydration of treated light oils, the aqueous tank bottoms of stored caustic treated and washed gasolines, vessel and tower washings at times of shutdowns and miscellaneous sources.

The alkaline waters referred to above, originating from continuous treating processes, contribute to the general pollution load but do not create a major problem. The intermittent discharge of aqueous tank bottoms and the washing of towers and vessels at times of shutdown can cause pollution peaks requiring special attention. At one refinery where biological treatment is to be provided for the plant effluent, intermittent flows of alkaline water, such as washings from batch treaters and shutdown drainage, will be discharged to holding tanks from which they can be drawn to the sewer at a controlled rate. The characteristics of shutdown drainage from a caustic methanol sweetening unit are shown in Table 4, column 6.

Special Chemicals. Under the category of special chemicals are included the special solvents and extraction solutions utilized in selective solvent refining, gas purification, light oil treating, etc., and the chemicals, by-products and wastes produced in the manufacture of petrochemicals.

Special chemicals utilized in petroleum processing include phenol, creosols, furfural, salts of isobutyric acid, nitrobenzene, acetone, methyl ethyl ketone, B.B. dichlorethyl ether, ethylene dichloride, benzol, tannin, fatty acids, diethanol amine, methanol, toluol sodium hypochlorite, trisodium phosphate, lead sulfide, copper chloride, etc. Special chemicals manufactured include various synthetic detergents, methanol, maleic anhydride, phthallic anhydride, benzol, toluol, naphthenic acids, etc.

The special chemicals mentioned above pose special waste control problems. The water soluble organics, for example, can add tremendously to the oxygen demand characteristics of the plant wastes if allowed to discharge into the sewers. Others listed are emulsifying agents and would adversely affect separator operation if allowed to mix with other refinery wastes. In many cases, the value of these materials is sufficient to justify the use of collection and recovery systems. Drainage from leaks, spills, pumps, valves, sampling, routine maintenance activities, etc., is frequently recovered to control losses to a minimum. Distillation facilities for the concentration and/or separation of chemicals from undesirable contaminants are generally provided. Furfural, for example, has been recovered for reuse by the use of two azeotropic distillations.

When recovery of these materials is impractical, they can generally be

removed from water by one or a combination of the procedures previously discussed in connection with the treatment of other wastes. Pilot-plant studies on the biological filtration of methyl ethyl ketone wastes indicated that reductions of 78 per cent or more could be expected for concentrations up to 60 ppm at temperatures of 80°F or above.²⁶ The hydraulic rate for these studies was 15 mgad forward flow and 1.4 volumes recycle for each volume of forward flow. The characteristics of waste water from units manufacturing and drying petrochemical detergents are shown in Table 3, columns 17 and 18 respectively.

Waste Gases. The waste gases from petroleum refining are stack gases from furnaces and reactors, hydrogen sulfide and sulfur dioxide. Except that stack gases may be used in waste treatment processes or may be scrubbed with water for solids removal they do not enter into water pollution control problems.

The acid gases, hydrogen sulfide and sulfur dioxide, may cause water pollution control problems. Hydrogen sulfide as produced from the distillation of crude and other processing is a contaminant to other refinery gases, i.e., methane, ethane, etc. The removal of hydrogen sulfide from liquid and gaseous hydrocarbon streams creates waste waters of highly obnoxious characteristics. These wastes have been discussed in detail in the section on Waste Caustics.

The conversion of various sulfur compounds in petroleum stocks to hydrogen sulfide followed by the removal and utilization of the hydrogen sulfides affords a means of reducing pollution due to sulfides. In several cases, hydrogen sulfide is converted to sulfur by the following reactions:²⁸



From 1 to 2 pounds of steam can be generated per pound of sulfur recovered in this process.

If contact acid manufacturing facilities are available it is possible to use hydrogen sulfide as a raw material in the manufacture of sulfuric acid. This use of hydrogen sulfide at one refinery enables the production of acid equivalent to 9 per cent of the requirements of the refinery. The acid thus produced is equivalent to about 0.1 ton of acid per 1,000 barrels of crude oil charge.

Sulfur dioxide is produced from stack gases, sulfuric acid concentrators, liquid sulfur dioxide refining units and sulfuric acid treating units. Normally sulfur dioxide wastes are discharged to the atmosphere. However, not infrequently atmospheric pollution problems must be corrected and the corrective measures create water pollution problems. The utilization of sulfur dioxide for the recovery of sulfur offers the best long term solu-

tion to the problem of pollution abatement. In some cases the conversion of treating facilities from batch to continuous may aid appreciably in reducing the magnitude of the local problem.

Sludges and Solids. Sludges, as referred to herein, may accumulate at the bottom of various crude or product storage tanks; as the result of various treatment processes; at the bottom of cooling towers and as the result of process and waste water treating.

Solids, as referred to herein, include coke, waste catalysts, filtering clays, slag, tank bottoms, etc.

Disposal of sludges and solids to the plant sewers is highly objectionable because of the effect of solids on oil separation.

Tank bottom sludges vary greatly in their characteristics, e.g., from an easily pumpable fluid to a set solid. In general these wastes may be treated for oil recovery or burned as fuel. Sometimes for the purpose of tank cleaning it is advantageous to flush these materials from the tanks using water. In some cases water flushing will create emulsions and suspensions that will produce unsatisfactory waste water effluents. The use of water flushing should be avoided as much as possible.

The use of water flushing in the cleaning of tanks storing leaded gasoline has produced obnoxious waste waters. Studies conducted at one refinery during the cleaning of a 100-foot diameter tank showed that a total of 26.7 pounds of dissolved lead and 4,571 pounds of total lead were discharged from the plant during the cleaning. Concentrations varied considerably depending on the operation. Maximum lead concentrations of 12.4 ppm dissolved and 3,730 ppm total were noted in the waste water at the cleaning site. Maximum concentrations of 3.4 ppm dissolved and 51.8 ppm total lead were found in the plant separator effluent. The use of water flushing for this tank cleaning operation is not recommended.

One of the major sources of sludge of high pollutorial characteristics is the acid treatment of refinery stocks. The handling of this material has been discussed in the section on Acid Wastes.

Sludge accumulating at the bottom of cooling towers is generally adaptable to disposal as fill. However, the problem of removing the sludge from the tower basin and the transfer of the material to the point of final disposal poses numerous problems.

Sludge from the clarification of water for process use poses the same type of problem as that of cooling tower sludge.

Sludge from the softening of water may be utilized, in some cases, for the neutralization of acidulous waters or as a coagulant aide in waste water treatment. Such a use is indicated in Figure 2.

Oil separator bottom sludges have characteristics as shown in Table 3, columns 4, 5 and 6. The quantity of sludge produced at one refinery varies

from 119 to 710 pounds of dry solids per million gallons of waste water. The characteristics of the sludges are such that they may be dewatered and burned with the production of heat in excess of that required for drying.

At a refinery along the Mississippi River, separator bottoms are air blown to remove oil. From 60 to 80 barrels per day of oil are recovered from approximately 500 barrels of silt. The remaining solids are sufficiently clean for disposal as fill.⁸

In some cases the sludges may be satisfactorily disposed of as fill. Precautions must be taken, however, to assure the fact that oil is not washed from the sludge to create water pollution.

Sludge obtained from the flocculation of refinery wastes has characteristics as shown in Table 3, column 8. These sludges may be disposed of by lagooning, drying on beds, dewatering and incinerating, spray drying and incinerating, etc. These methods have been discussed in more detail in the section on Emulsions.

Sludges resulting from the treatment of slop oils by heat and spent caustic have characteristics as shown in Table 3, column 9. Normally this material is periodically drawn from the treating tanks to ponds where it becomes dewatered sufficiently for burning as fuel. Pilot plant studies by the authors indicated that this sludge could be filtered on a vacuum precoat filter. Filter rates were low, however, about 1 gallon per square foot per hour on the average. The oil recovered required additional settling to meet the required specifications. The heat content of the filter cake was in excess of that necessary to maintain combustion.

Cooling Water. Cooling water makes up nearly the entire volume of waste water from petroleum refining operations. Since these wastes may become oil-contaminated due to equipment failure it is necessary to provide oil separation facilities as insurance against accidental pollution. Consequently, uncontaminated cooling water is generally turned into a common oil carrying sewerage system. However, when the standards of waste-water quality necessitate costly "effluent polishing," the separate collection and disposal of cooling waters which are subject to infrequent pollution has proved economical at some refineries. Likewise, the size of effluent treatment facilities has been substantially reduced by decreasing the quantity of waste water through the use of recirculating cooling systems. At one refinery requiring effluent treatment, the quantity of waste water has been reduced from 24 mgd to 8 mgd by the installation of cooling towers. The use of dirty water cooling tower systems and the elimination of barometric condensers and jet vacuum pumps as discussed in the section on Emulsions also serve to keep sizes of treatment facilities at a minimum. Where water is scarce, refineries have used sewage treatment

plant effluents as a source of water supply² and in other cases have used their own treated effluents.¹⁴

Sanitary Wastes. Sanitary wastes offer no opportunity for waste utilization. The wastes may be discharged to refinery or municipal sewerage systems or to separate sewerage and disposal facilities. Discharge to refinery sewerage systems is not in agreement with good public health practice and may interfere with efficient oil separation. However, this has been done in several cases where the effluent treatment facilities are equivalent to those required for the secondary treatment of sanitary sewage. When separation of sanitary wastes from an existing combined system is required, costly sewer construction is usually involved due to the unavoidably wide distribution of the sanitary facilities and the maze of underground process piping.

Transportation and Marketing

Wastes resulting from the transportation of crude oil and refined products and the marketing of petroleum products include oil from leaks in transportation, transferring and storage equipment, from spills occurring during transferring operations, from bilge, ballast and wash water from tankers and barges, from the cleaning of tank trucks and tanks, from sales stations operations and from other related activities.

Oil pollution from leakage of transportation facilities may be general in distribution, but is usually negligible in quantity for mobile units, but can be relatively serious and localized for pipelines. Oil leaks from pipelines and underground storage tanks have in some cases polluted ground water used for drinking water supplies. The loss of oil causing such pollution is very costly. Consequently, considerable effort is made to prevent such losses by the application of proper materials and methods of construction and modern corrosion prevention technique.

Pollution at marine terminals, railroad sidings and truck terminals has been appreciably reduced by the installation of protective curbings, pans, collection lines, storm water separators, etc., to retain and recover oil.

Oil contaminated bilge water, ballast water and ship cleaning wastes can be discharged at sea when weather conditions permit. However, many docks and refineries are equipped with treatment facilities so that these wastes may be pumped ashore and the oil recovered. In New York harbor, a private concern operates barges which receive bilge and ballast water from incoming ships and transport it to a reclamation plant where the oil is recovered for sale. A special raft has been designed to function as an oil separator for bilge and ballast water, retaining the oil for reclamation and discharging the oil free water.³⁰ Oil separators are manufactured for use on ships to separate oil from bilge water.

Waste produced in the washing and maintenance of tank trucks is milky in appearance and may be high in both oil and BOD content. It may contain considerable quantities of fiber, silt and grit, free and emulsified oil, soluble soap and insoluble soap curd. While the quantity of these wastes from a truck terminal is relatively small, the location of the terminal on streams used for agricultural or recreational purposes usually requires a high degree of waste treatment. This is also true of the cleaning of tanks at distribution terminals. A miniature coagulation and sedimentation plant for breaking truck washing wastes is in use by one oil company.³¹ Tank cleaning wastes from one terminal are transported about 30 miles by tank truck to the refinery for disposal. Wastes from the cleaning of tanks storing leaded gasolines require special handling due to the toxic nature of tetraethyl lead. Solids removed from these tanks are usually buried and the area designated by suitable warning signs. After the tetraethyl lead has decomposed as indicated by periodic tests, the ground may again be made available for other uses.

Waste oil originating at sales stations consists primarily of used crank case oil. This material together with a small additional quantity from leaks and spills is collected and may be disposed of in a number of ways. Various disposal methods include use as a fuel in municipal garbage incinerators, reprocessing and resale, use in mosquito control, use in oiling dirt roads, and many others. Disposal of waste oil in this manner is usually done by contract with private concerns or municipalities. The discharge of this material to the sewers or disposal on dumps is not recommended.

References

1. Weston, R. F., and Hart, W. B., "The Water Pollution Abatement Problems of the Petroleum Industry," *Water Works and Sewerage*, **88**, No. 5, 208 (1941).
2. Weston, R. F., "The Waste Disposal and Utilization Problems of the Petroleum Industry," Proc. First Ind. Waste Utilization Conference, Purdue University (1944).
3. Stevenson, H. L., "Profits from Oil-Field Wastes," *Oil Weekly*, **120**, No. 4, 34 (1945).
4. Logue, B. W., "Oklahoma Oil-Field Brines and Their Utilization," *Oil and Gas J.*, Feb. 11, p. 49 (1943).
5. Morris, W. S., "Disposal of Oil-Field Salt Waters," Proc. 5th Ind. Waste Conference, Purdue University (July 1950).
6. D'Arcy, Nicholas A., Jr., "Dissolved Air Flotation Separates Oil from Waste Water," *Oil and Gas J.*, **50**, No. 27, 319 (1951).
7. Operating Data, Ballast Wharf Treatment Facilities, Atlantic Refining Company, Philadelphia, Pa. (1949).
8. Weston, R. F., Separation of Oil Refinery Wastes, *Ind. Eng. Chem.*, **42**, 607 (1950).

9. Waste Control, Atlantic Refining Company, Philadelphia, Pa. (1951). Unpublished Data.
10. Gurwitsch and Moore, "The Scientific Principles of Petroleum Technology," pp. 452-64, New York, D. Van Nostrand Co., Inc. (1932).
11. Shindler, H., "Treating Refinery Chemical Waste," *Petroleum Processing*, 6, No. 5, 492 (1951).
12. Camp, E. Q., "Refinery Wastes," Humble Oil Company, Baytown, Texas.
13. Proctor, E. M., "Reduce Oil Content of Refinery Effluent by Treating Emulsions Separately," *Petroleum Processing*, 5, No. 2, 132 (1950).
14. F. M., McCann, D. L., and Bedell, H. L., "A Method of Conditioning of Refinery Effluent for Re-Use and Disposal Faulconer," Presented, 14th Mid-Year Meeting, Division of Refining, American Petroleum Institute (April 7, 1949).
15. Ashley, J. H., "Underground Water Pollution Abatement in Los Angeles," *Water and Sewage Works*, 97, No. 7, 297 (1950).
16. Gibbs, F. S., "Unique Flotation Unit for Industrial Waste Treatment," *Water and Sewage Works*, 97, No. 6, 241 (1950).
17. Weston, R. F., Merman, R. G., and DeMann, J. G., "The Coagulation of Refinery Wastes using Twin Pilot Plant Units," Proc. Ninth Annual Water Conference, Engineer's Society Western Pennsylvania, Pittsburgh, Pa., p. 151 (1948).
18. Teague, J. U., "Economics of Controlling Water Produced with Oil," *Oil and Gas J.*, p. 125 (Nov. 14, 1950).
19. Borroughs, L. C., and Carnahan, R. W., "Disposal of Spent Chemicals from Petroleum Refining," Presented, 14th Mid-Year Meeting, Division of Refining, American Petroleum Institute (April 7, 1949).
20. Albright, J. C., "Recovery Usable Water from Waste by Extracting Condensable Gases," *Petroleum Processing*, 3, No. 11, 1116 (1948).
21. "Manual on Disposal of Refinery Wastes," Vol. III, Chemical Wastes, Second Ed. American Petroleum Institute, Division of Refining (1951).
22. Nelson, W. L., "Petroleum Refinery Engineering," New York, McGraw-Hill Book Company, Inc. (1941).
23. Bland, William F., "How to Conserve Sulfuric Acid," *Petroleum Processing*, 6, No. 8, 865 (1951).
24. Gothard, N. J., and Fowler, J. A., The Pollution Abatement Program of the Sinclair Refining Company, East Chicago, Ind.
25. Weston, R. F., and DeMann, J. G., "Factors Promoting the Biological Oxidation of Industrial Wastes," Presented, 110th Meeting, Am. Chem. Society, Chicago, Ill. (September 11, 1946).
26. Degnan, J. M., Merman, R. G., and DeMann, J. G., "Pilot Plant Investigations of the Biological Filtration of Petroleum Refinery Wastes," Presented at Seventh Industrial Waste Conference, Purdue University (May 7-9, 1952).
27. Baker, R. A., Degnan, J. M., and Weston, R. F., "Pilot Plant Studies of the Biological Treatment of Petroleum Refinery Wastes," To be presented, 24th Annual Conference, Pennsylvania Sewage and Industrial Wastes Association (Aug. 27-29, 1952).
28. "Sulfur Produced from Hydrogen Sulfide," *Petroleum Refiner*, 29, 225 (Sept. 1950).
29. Bragg, Charles G., "Fertilizer from Refinery Wastes," *Petroleum Processing*, 7, No. 4, 502 (1952).
30. Anon., "Raft for Separating Oil and Ballast Water," *Oil and Gas J.*, 44, No. 46, 79 (1946).
31. Weston, R. F., "Miniature Industrial Waste Treatment Plant," *Water and Sewage Works*, 94, No. 3, 111 (1947).

16. Treatment and Disposal of Liquid Radioactive Wastes

Conrad P. Straub

Sanitary Engineer, Environmental Health Center, Public Health Service, assigned to the Health Physics Division, Oak Ridge National Laboratory

Radioactive wastes are similar to chemical wastes, thus in general the methods of removal are similar to conventional processes used in the treatment of chemical wastes. However, in dealing with radioactive wastes our scope must be broadened to include the concept of radioactivity along with the chemical, bacterial, biological and general physical parameters that have been used in defining waste characteristics. Only time can modify radioactivity; no known physical, chemical or biological process can speed up or slow down the emanation of particles and rays from radioactive atoms.

In this discussion the following points will be considered:

- (1) Sources, nature and quantity of wastes.
- (2) Treatment techniques.
- (3) Procedures for measuring radioactivity (instrumentation).
- (4) Health hazards and pollutional effects of the wastes.

Because information on many of the operations in the atomic energy field, particularly those relating to processing, separation and production, are not available to the public for reasons of national security, this discussion will be restricted to information that is readily available either in the open periodical literature or from the Atomic Energy Commission (AEC).

SOURCES, NATURE AND QUANTITY OF WASTES

There are several sources of radioactive wastes: (1) Nuclear reactors and separation plants. (2) Disposal of radioisotopes used in research, medicine and industry. (3) Detonation of a nuclear bomb. (4) Natural radioactivity in water. (5) Power piles (similar to 1).

Nuclear Reactors and Separation Plants

Perhaps the largest single source of radioactive liquid wastes is that from cooling the reactors as at Hanford, where treated Columbia River water is used. In passing through the pile there is enough activity induced in the once-circulated waters to make direct return of the wastes to the Columbia River inadvisable. It has been reported⁷ that the volume of water diverted from the Columbia River to cool the Hanford reactors would equal the water consumption of a city of over 1.5 million inhabitants.

Fuel elements removed from the pile are highly radioactive, giving off penetrating radiations which are damaging to living tissues. This radioactive material is processed chemically for separation of the more valuable fission products. Because of the very high levels of radioactivity encountered it is necessary to carry on these operations by remote control using specially designed hoods and equipment. Specifications for the design of radiochemical laboratories have been published.^{13,16,28}

At the Oak Ridge National Laboratory certain fission products of value are removed by chemical processing. These separated materials are the radioisotopes that are shipped for research, medical and industrial use. The residue from the process is discharged to tanks and stored to take advantage of natural decay to reduce the radioactivity of the waste.

Few data are available on the volumes of wastes produced, however, some data have been reported recently for Oak Ridge National Laboratory² and for Brookhaven National Laboratory⁹ and are summarized in Table 1.

Use of Radioisotopes in Research, Medicine and Industry

During the past few years radioisotopes have found wide use in research, medicine and industry. The extent of their use is indicated by the number of shipments made from Oak Ridge National Laboratory since July 1947 and is shown in Figure 1. Since the inception of the program 19,427 shipments of radioisotopes totaling 1651.6 curies have been made to off-Commission (non-AEC), Commission (AEC) and foreign recipients.

In general, small amounts (microcurie* and millicurie* quantities) of radioactive materials are used in tracer experiments, and the wastes resulting from their discharge are small in volume and low in activity. Larger quantities, both in volume and activity, may be discharged from

*The curie is used as the standard unit in measuring the activity of a radioactive substance and is taken as equal to 3.7×10^{10} disintegrations per second (dis/sec). A millicurie, mc (1/1,000 curie), is equivalent to 3.7×10^7 dis/sec, and a microcurie, μ c (1/1,000,000 curie) is equivalent to 3.7×10^4 dis/sec.

TABLE 1. TYPES AND VOLUMES OF WASTES PRODUCED AT TWO NATIONAL LABORATORIES^{2,9}

Installation	Types of Waste	Volume (gals/week)
Oak Ridge National Laboratory	(1) Metal. Contains dissolved compounds of uranium. This waste must be collected, concentrated, and stored for recovery processes. It is nearly always quite radioactive, requiring special precautions in handling and storing.	
	(2) Radiochemical. Composed of highly radioactive fission products and various chemical by-products from the production and developmental processes of the Laboratory.	50,000
	(3) Process. Large volume waste composed mostly of cooling water and non-radioactive chemical by-products.	5,000,000
Brookhaven National Laboratory*	(A) Metal. Contains accountable uranium and fissionable material.	150
	(B) Chemical. High activity waste containing no accountable material.	615
	(C) Solvent. Contaminated waste which cannot go through waste system because of volatile solvents of HCl content.	75
	(D) Chemical. Low activity waste which requires no shielding.	5,770
	(E) Uncontaminated. Waste which is monitored for activity before disposal.	77,000

*Rough estimated values used in designing system and probably high. Converted from yearly figures by dividing by 52.

hospitals³ where radioisotopes are finding widespread use as therapeutic agents.

Other Sources

Radioactive materials will be released in the detonation of a nuclear bomb, and may result in the production of wastes which will have to be treated. The effects of an atomic bomb blast have been adequately covered.¹⁴ According to Love,¹⁵ the only natural occurring radioactive elements likely to be present in measurable amounts in water are uranium-238, radium-226 and thorium-232. The maximum activity reported for a ground water source—a spring in Shimane, Japan—is $709,000 \times 10^{-12}$ grams of radium per liter (which is equivalent to 1,570 dis/min/ml).

What the future holds for the development of atomic power cannot be forecast with any degree of certainty. However, if such plants become a reality, it is quite probable that the waste disposal problem will be increased many-fold.

REMOVAL AND DISPOSAL OF RADIOACTIVE CONSTITUENTS

Treatment methods for the removal of a single radioelement may be based upon the chemistry of that particular element. However, when

a waste contains a mixture of radioisotopes, as in the case of mixed fission products, removal of the elements responsible for the radioactivity becomes more difficult and it may be necessary to resort to a series of unit processes to reduce the activity to acceptable tolerance concentrations before discharge. This difficulty points to the advisability of treating the wastes as close to their source of production as practicable. Thereby, it

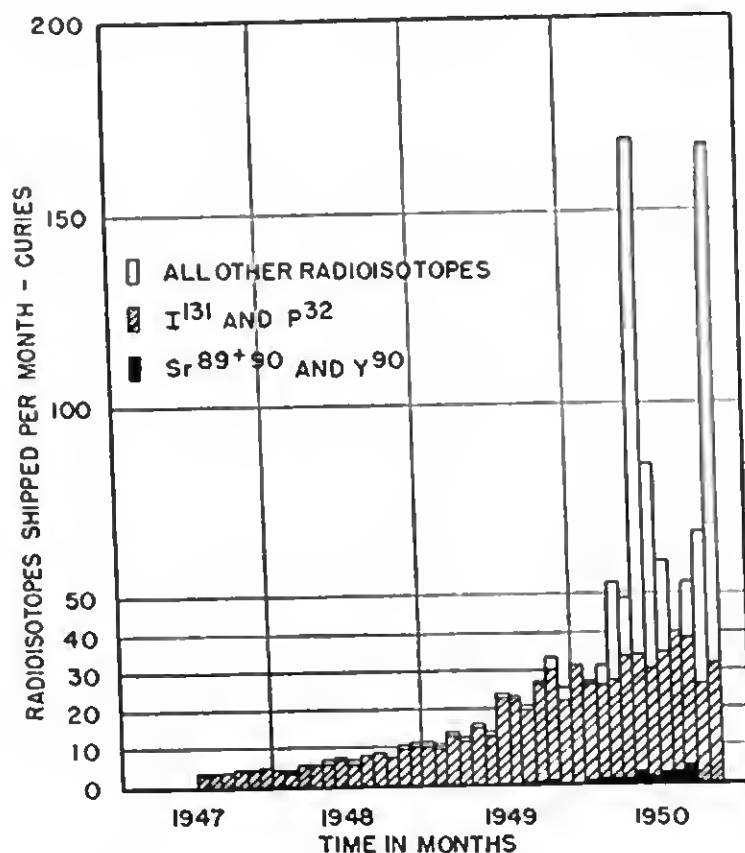


FIGURE 1. Number of curies of radioisotopes shipped monthly by the Operations Division, Oak Ridge National Laboratory, for the period July 1947 through December 1950

may be possible to eliminate admixture with radioisotopes that are discharged in other processes, thus simplifying the treatment and removal of the objectionable materials.

The discharge of wastes into sewerage systems and watercourses should not be permitted nor practiced until it has been ascertained that no public health or radiation hazard will be produced as a result of such discharge. Little information is available concerning the processes involved in the concentration of radioactive substances by specific muds and soils, by benthos in the stream, by plankton and by other flora and fauna which may spend part or all of their life cycle in the receiving waters.

Of the methods known to sanitary engineers and chemists for treating and disposing domestic and industrial wastes, the following have been suggested as possible modes of attack in solving problems incident to the treatment and disposal of radioactive wastes (these are arranged in the order of their importance and use):

- (1) Dilution
- (2) Evaporation
- (3) Carrier precipitation (coagulation or co-precipitation)
- (4) Ion exchange (natural clays and synthetic resins)
- (5) Biological processes
- (6) Metallic displacement
- (7) Sand filtration
- (8) Crystallization
- (9) Solvent extraction
- (10) Electrolytic separation
- (11) Differential volatility
- (12) Electrodialysis

Disposal by Dilution

Disposal by dilution may take place in two forms, liquid or chemical. The former is well known and requires no amplification except to state that discharges must be kept below maximum permissible concentration values (see Table 11, p. 468).

Disposal by chemical dilution is somewhat more novel, and involves dilution with a carrier having chemical characteristics identical to those of the radioactive substance itself. The method is based upon the principle that the body (or any living form) does not distinguish between isotopes of the same element. Hence, since it can accept only certain concentrations of specific nontoxic substances, excesses will be excreted or discharged, the radioactive form of an element may be diluted with its stable isotope to such a concentration that when taken into the body the amount of the radioactive form retained will be below the maximum permissible concentration. This is one means of reducing the possible effects of reconcentration by lower forms before discharge of the waste into the environment. An example of this type of dilution and its effect is that of the addition of carrier-KI on the removal of I^{131} by trickling filters.

Evaporation

For the concentration of large volumes of wastes containing small amounts of radioactive materials, evaporation, although expensive, will remove practically all of the activity from the liquid fraction and will concentrate that activity in the solid residue or slurry. To permit disposal

in this form as a means of reducing the amount of space required for storage, evaporation is desirable.

In June 1949, a waste evaporator was placed in operation at Oak Ridge National Laboratory which, with auxiliary equipment, is engaged in concentrating the radioactive components of the radiochemical waste for storage. The waste evaporator (Figure 2) is a simple, pot-type, internal

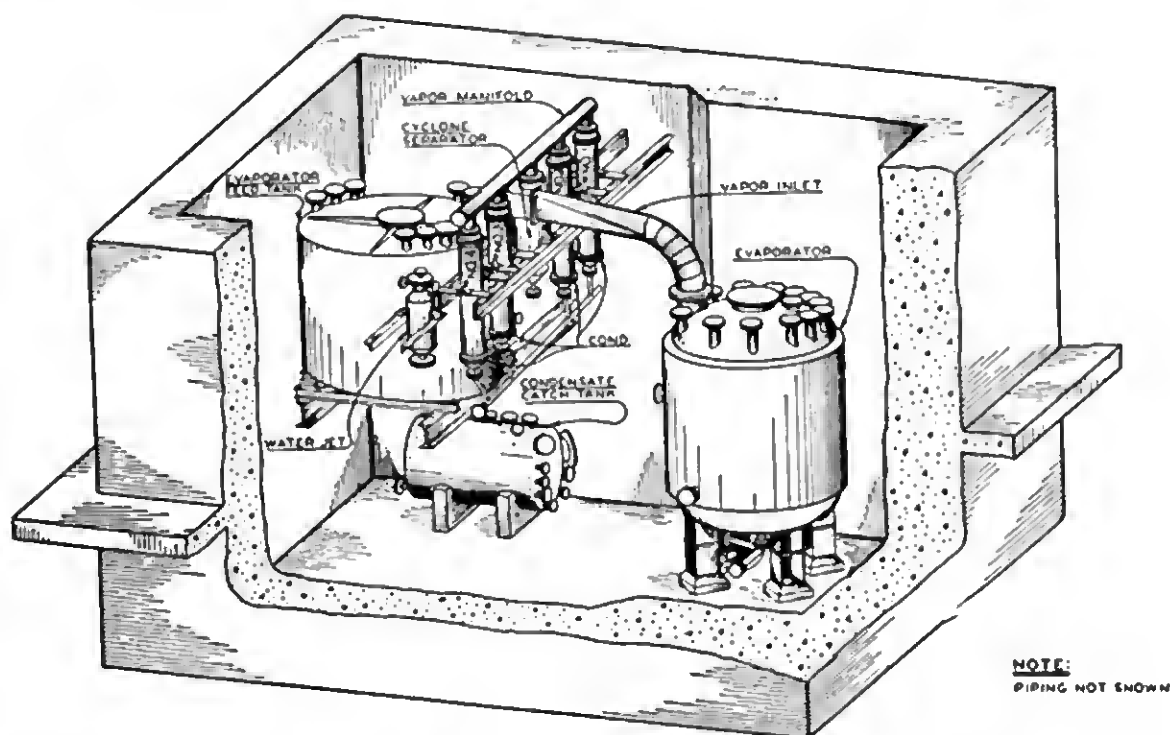


FIGURE 2. Schematic drawing of Oak Ridge National Laboratory waste evaporator

steam-coil heated unit housed in a shielded concrete building and has a design capacity of 300 gallons of water per hour. Decontamination factors* of 10^5 have been demonstrated² with volume reductions of about 60 to 1. Evaporator foaming is the only serious operating problem so far reported.²

McCullough¹⁷ has described the evaporator installation at the Knolls Atomic Power Laboratory, Schenectady, New York, which treats dilute wastes containing alpha- and beta-gamma activity. It is reported that the evaporator system is capable of decontamination factors of 10^7 . Cost analyses have been made and show that with two-shift operation at the design rate of 125,000 gal/month the cost was \$0.138 per gallon and with three-shift operation the total cost would be \$0.114 per gallon.

$$\text{*Decontamination factor} = \frac{\text{Influent counts or dis/min/ml}}{\text{Effluent counts or dis/min/ml}}$$

Decontamination factors of the same order of magnitude have been reported for the evaporator installation at Brookhaven National Laboratory.

Carrier Precipitation

Carrier precipitation (co-precipitation or coagulation) is used extensively in the treatment of many industrial wastes and has been adapted to the removal of certain radioactive materials. In the removal of arsenic, antimony, molybdenum, selenium, tellurium and cerium, coagulation has been applied with varying success. With ruthenium and plutonium, however, removals have been very satisfactory. In many instances it has been found that coagulation was most effective at high pH values, in the ranges normally encountered in the chemical softening of water. Studies have been made at Oak Ridge National Laboratory in which routine and special coagulation techniques have been applied to the removal of specific radioisotopes from "spiked" water solutions.

Using routine alum and lime coagulation, Placak and Lyle, as reported by the writer,²⁷ obtained removals of specific radioisotopes as shown in Table 2. The data show that alum coagulation was effective for the removal of P^{32} , Y^{91} (when the proper alkaline agent, Na_2CO_3 , was used), Ce^{144} and Y^{90} , and that the procedure was ineffective for the removal of I^{131} , Sr^{89} and Sr^{90} . Essentially similar results were obtained with iron as the coagulant.

TABLE 2. ALUM COAGULATION RESULTS*²⁷

Element	Removal (%)	Remarks
I^{131}	Up to 10	Addition of small amounts Cu, Ag, or C increases removals to 75%
P^{32}	98 plus	
Sr^{89}	10	Increasing turbidity from 50 to 1,000 ppm increased removal efficiencies to 50%
Y^{91}	45	Using NaOH as alkali
	98	Using Na_2CO_3 as alkali
	17-82	For turbidity ranges 50-1,000 ppm
Ce^{144}	98	
	70-86	For turbidity ranges 50-1,000 ppm
Sr^{90} - Y^{90}	98 for Y	On standing more of the Y daughter formed from Sr
	10 for Sr	

Essentially similar results were obtained using iron as a coagulant.

*Placak and Lyle, 1950 as reported by Straub.¹¹

Since the number of highly insoluble phosphates exceeded the number of insoluble hydroxides, Lauderdale¹² carried out experiments in which he employed a modified coagulation technique. Tracer type runs were made

with isotopes of cerium, strontium, zinc, yttrium, antimony and tungsten, which were added to distilled water, with the floc being formed by mixing

TABLE 3. RESULTS OF PHOSPHATE COAGULATION STUDIES¹²

Isotope	Coagulant	Mg/Liter Coagulant	Removal (%)
Ce ¹⁴⁴	KH ₂ PO ₄	200	99.8
Ce ¹⁴⁴	Na ₃ PO ₄	120	99.9
Sr ⁸⁹	KH ₂ PO ₄	100	81.3
Sr ⁸⁹	Na ₃ PO ₄	240	97.8
Y ⁹¹	KH ₂ PO ₄	100	99.9
Sb ¹²⁴	KH ₂ PO ₄	100	66.1
Sb ¹²⁴	Na ₃ PO ₄	120	67.4
Zn ⁶⁵	KH ₂ PO ₄	50	99.6
W ¹⁸⁵	KH ₂ PO ₄	200	10.7

Ca(OH)₂ and either KH₂PO₄ or Na₃PO₄ at a pH of approximately 11.5. Some typical results for one-stage batch treatment are indicated in Table 3. Essentially complete removals of Ce¹⁴⁴, Y⁹¹ and Zn⁶⁵ were obtained by phosphate coagulation.

When compared with similar data using alum and ferric hydroxide as the precipitant, phosphate treatment in every instance produced a greater concentration of radioactive elements in the settled floc. These data in terms of decontamination factors are reported in Table 4.

TABLE 4. DECONTAMINATION FACTORS FOR Y, CE AND SR USING DIFFERENT COAGULANTS¹²

Isotope	Alum	FeCl ₃	KH ₂ PO ₄	Na ₃ PO ₄
Y ⁹¹	20	1.1	1000	—
Ce ¹⁴⁴	11.1	22.7	500	1000
Sr ⁸⁹	1.1	1.02	5.3	45.5

$$\text{Decontamination Factor (D.F.)} = \frac{\text{initial counts/min/ml (c/m/ml)}}{\text{final counts/min/ml (c/m/ml)}}$$

Because of the variation found in the removal of Sr⁸⁹, this radioisotope was selected for further study of the variables involved, that is, pH, phosphate to calcium ratio and quantity of floc. The effect of the Na₃PO₄ to Ca(OH)₂ ratio and pH is shown in Figures 3 and 4. At a ratio above 2.2 to 1 and above a pH of 11.3 little change in the removal of strontium was noted.

Further runs were made using phosphate precipitation to treat wastes containing mixed fission products. Typical results are given in Table 5.

Summarizing Lauderdale's work on phosphate coagulation¹² we may say that under the test conditions described:

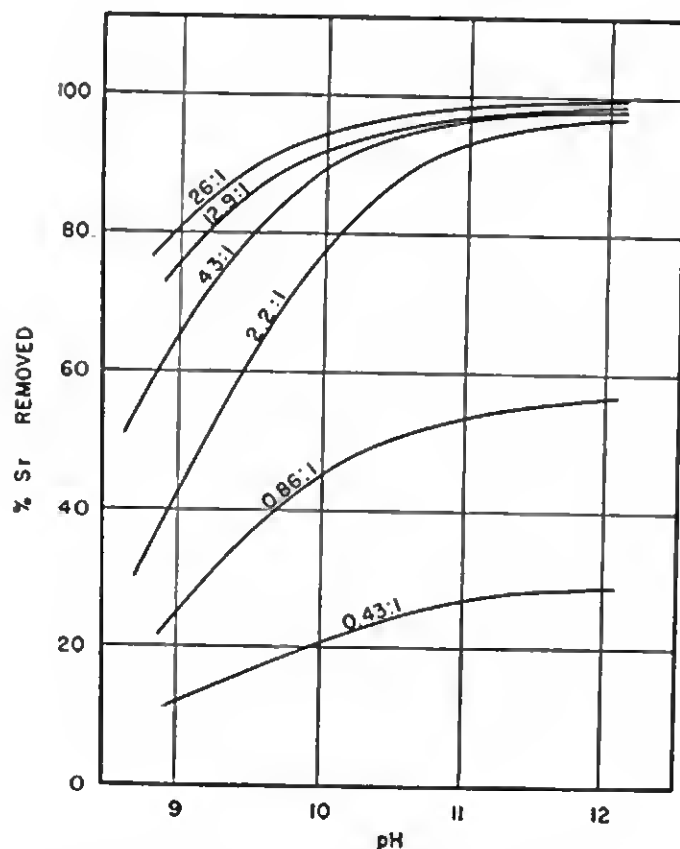


FIGURE 3. Per cent of Sr^{89} removed from solution as a function of pH for different values of mg. Na_3PO_4 to mg. $\text{Ca}(\text{OH})_2$

TABLE 5. TREATMENT OF MIXED FISSION PRODUCTS BY PHOSPHATE PRECIPITATION¹²

Test	Stage	Treatment	Initial c/m/ml*	Final c/m/ml	Decontamination Factor	Removal (%)
VI	1	100 ppm clay 100 ppm Na_3PO_4	4,810	31	155	99.3
VII	1	100 ppm clay 100 ppm Na_3PO_4	2,150	27	80	98.8
	2	100 ppm $\text{Ca}(\text{OH})_2$ 100 ppm Na_3PO_4		18	120	99.1
VIII	1	100 ppm clay 100 ppm Na_3PO_4	2,935	12	245	99.7

*c/m/ml = counts/min/ml.

(1) Essentially all the Ce^{144} , Y^{91} and Zn^{65} could be removed and elements with like chemical properties would probably show similar removals.

(2) Approximately 10 per cent of the W^{185} 65 per cent of the Sb^{124} and 95 per cent of the Sr^{89} could be removed.

(3) Decontamination factors greater than 100 (percentage removals in

excess of 99 per cent) could be obtained with fission product mixtures to which clay had been added.

(4) Greatest efficiencies occurred at high pH and excess of phosphate.

Using a 1,000 liter per day pilot plant which included mixing, flocculation, settling and filtration, the writer²⁷ studied the removal of P^{32} and I^{131} by conventional water treatment techniques (small dosages of

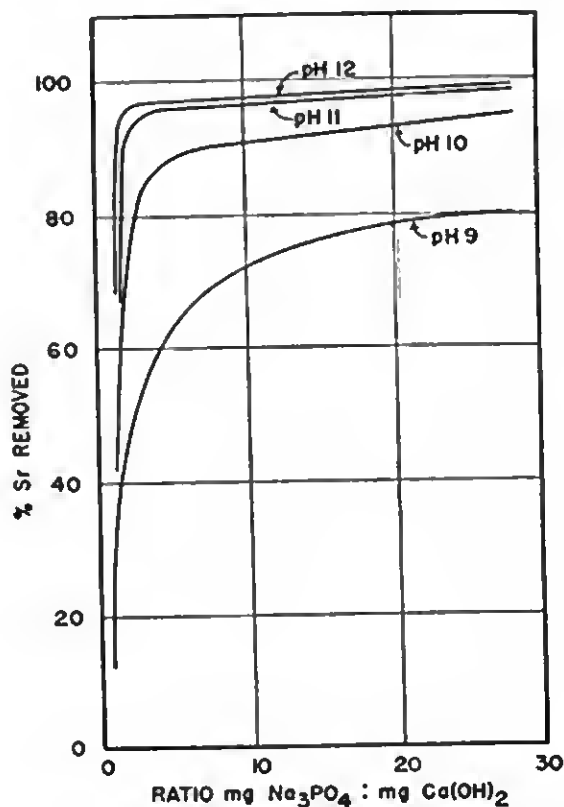


FIGURE 4. Per cent of Sr^{89} removed from solution as a function of the ratio of mg. Na_3PO_4 to mg. $Ca(OH)_2$ at pH values ranging from 9 to 12

coagulant-1 gpg). Removals obtained, along with results reported by others, are indicated in Table 6. Similar findings for the removal of P^{32} by conventional water treatment techniques have been reported in personal communications by a group at the Massachusetts Institute of Technology.

Preliminary studies on alkaline precipitation of a radioactive waste slurry made by the writer²⁶ show that the removal of radioactive constituents is dependent, among other factors, on the alkaline precipitant used (Figure 5). Similar findings were referred to in the case of Y^{91} in Table 2.

Newell *et al.*²² have reported the results of their studies at Los Alamos on the removal of plutonium from laundry wastes by chemical precipi-

TABLE 6. PILOT AND LARGE SCALE PLANT RESULTS (²⁷ AND OTHERS)

Isotopes or Test Material	Treatment	Removal (%)		Ref.
P ³²	Coagulation with alum, lime + sedi- mentation	85	27	
	Above + filtration	96-98	27	
I ¹³¹	Coagulation with alum, lime, sodium silicate + sedimentation	<1	27	
	Above + filtration	<1	27	
	Above + 5 ppm carbon	15	27	
	Above + carbon + filtration	25	27	
Mixed Fission Products ¹	Coagulation with alum, lime, sodium sili- cate + sedimentation	46		Straub, Brockett & Stepp*
	Above + filtration	70-73		Straub, Brockett & Stepp*
Mixed Fission Products ²	Coagulation with iron + sedimentation	86		Lindsten & Brockett*
W-6 Waste ³	Coagulation with iron + sedimentation	29		Lindsten & Brockett*

*Unpublished information.

¹ Mixed fission products to simulate conditions after a bomb blast but with increased percentages of Ru, I and Sr which are hard to remove.

² Simulates condition after bomb blast.

³ Dissolver solution represents potential waste from nuclear reactor.

tation. They found that best results were obtained with the addition of 300 ppm CaCl₂, NaOH to pH 12.0, 20 ppm sodium silicate, and 60 ppm of iron as ferrie chloride. Removals obtained are indicated in Table 7.

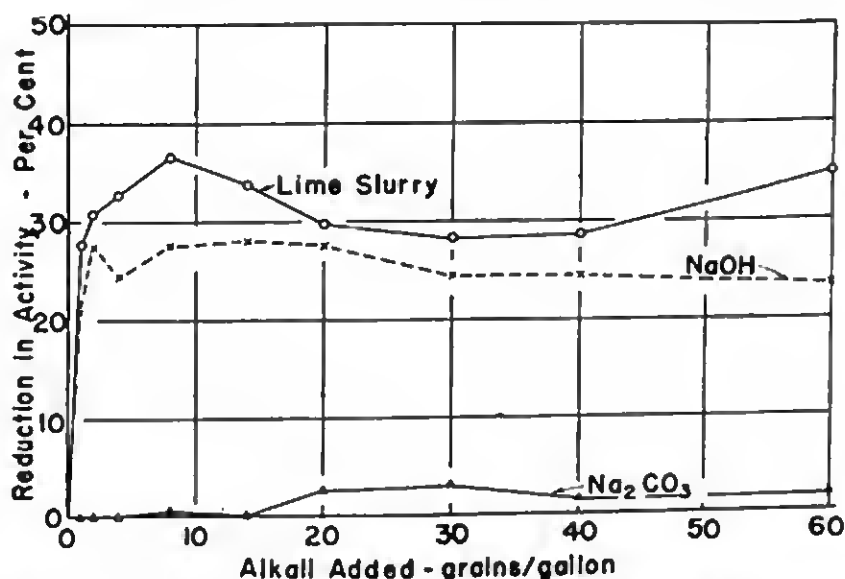


FIGURE 5. Removal of metal waste activity by alkaline precipitants

TABLE 7. REMOVAL OF PU FROM LAUNDRY WASTES BY CHEMICAL TREATMENT
Period of Observation—March 9 to June 9, 1949²²

	Suspended Solids ppm	% Ash	Settleable Solids ml/l	Plutonium Concentration c/m L*	
				Raw	Treated
Maximum	966	83	120	3,185	665
Minimum	150	29	20	176	4
Average	384	50	58.5	600	87

*c/m/L—counts/min/liter.

As shown 5.85 per cent of the original volume results in sludge and the problem involved in handling this amount of sludge suggests that other processes should be considered to eliminate this undesirable factor. Normally, chemical precipitation will produce 25 to 30 times the volume of sludge as that produced by trickling filters.

Ion Exchange (Natural clays and synthetic resins)

Where soil conditions are favorable some wastes may be discharged to underground cribs from which they will leach out gradually. It has been found that some radioactive contaminants will readily attach themselves to certain soils and thereby are held near the point of discharge, as at the Hanford Works, Washington. This method should not be resorted to unless the geology of the area is known to be favorable.

Jacobson and Overstreet¹⁰ reported in 1947 that little or nothing was known concerning the fixation by soils of plutonium and the products of nuclear fission and their adsorption by plants. Tests were conducted in which plutonium and the fission products strontium, yttrium, zirconium, columbium (niobium) and cerium were adsorbed on a bentonitic clay and a montmorillonitic type of sandy soil. The percentage of radioisotopes initially fixed on the clay are shown in Table 8.

TABLE 8. ADSORPTION OF CERTAIN FISSION PRODUCTS BY CALCIUM
BENTONITE AT pH
5.5 USING 100 MG OF CLAY PER LITER OF SOLUTION¹⁰

Element	Adsorbed (%)
Y	98.8
Ce	94.3
Zr + Nb*	98.5
Sr	60.4
Te	30.2
PuO ₂ ⁺⁺	18.6
Pu ⁺⁺	66.0
Pu ⁺⁺	94.2

*The Zr + Nb sample was an equilibrium mixture of the elements which had been isolated from a sample of fission products.

For the removal of radioisotopes from a solution containing about 95 per cent cesium and 4.5 per cent ruthenium, Lauderdale used kaolinitic and montmorillonitic clays as adsorbing agents. Although the dosages of clay required were very large, up to 50,000 ppm, removals of 80 to 85 per cent were obtained. In studies with evaporator waste slurry the writer²⁶ has shown that 80 to 88 per cent of the radioactivity could be removed by the addition of about 900 to 4,400 mg/l of clay as shown in Figure 6.

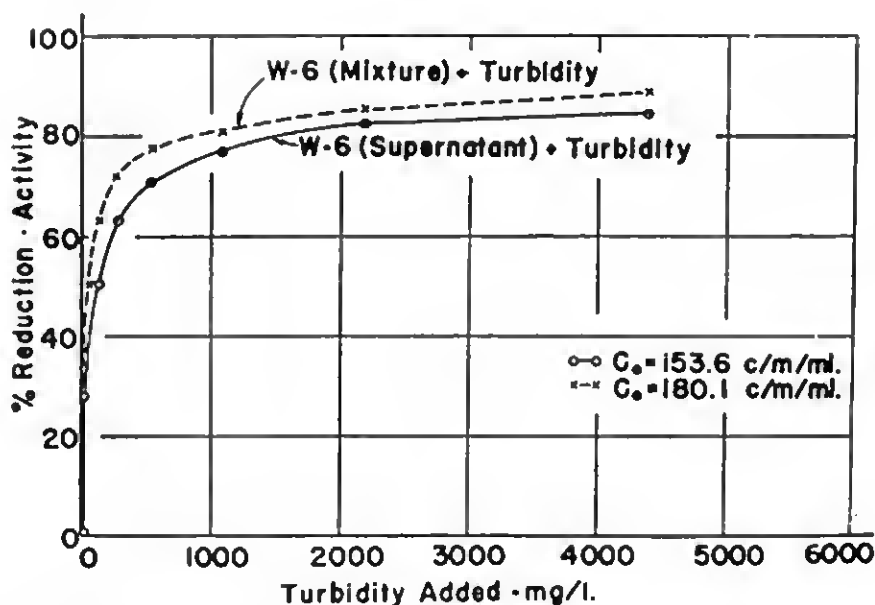


FIGURE 6. Removal of metal waste activity by adsorption on clays. C_0 = initial uncorrected concentration of radioactivity

Some interesting studies are underway at Brookhaven National Laboratory⁶ to develop a procedure for the permanent disposal of long-lived radioactive wastes by the assimilation of wastes on highly stable natural materials in the earth such as clays. Preliminary experiments have been made to determine the exchange capacity (milliequivalents per gram—me/gm) of three clay materials using Sr^{89} as the radioisotope. After assimilation on the clay the radioactive constituents were fixed to the clay particle by heat treatment at temperatures ranging from 300 to 900°C. Two of the three clay materials showed 100 per cent fixation for periods of 12 to 28 days (the length of the test in each instance) at temperatures of 750 to 880 and 875°C, respectively.

With the newer high capacity synthetic cation and anion exchange resins many radioactive elements may be removed from large volumes of dilute wastes. Data released by Ayres¹ show that sodium, barium, lanthanum and cerium are removed in cation exchange columns, and

that tellurium, molybdenum and ruthenium are removed in anion exchange columns. The work of others indicates that under suitable conditions strontium, cesium, cerium and other rare earths may be removed by cationic exchangers. Ion exchange columns may be used for the removal of single radioelements or combinations of certain radioisotopes in dilute solutions which are low in solids and may also be used as polishing units following the removal of gross radioactive contaminants by coagulation or carrier precipitation and filtration.

Lauderdale and Emmons¹¹ have used a mixed or monobed cation and anion resin bed to remove residual activity after passage through an iron scrub, burnt clay and activated carbon. They report that the mixed resin bed accounted for a removal of about two per cent of the initial activity applied from a one-month old solution and 11.3 per cent of the initial activity when a 60-hour iodine dissolver solution (after approximately 85 per cent of the iodine was extracted) was applied.

Biological Processes

Biological concentration of waste materials has caused some concern²⁹ as to whether it might be conceivable first to have concentration in algae, then in snails that live on the algae, then in fish that eat the snails, and consequently whether a concentration dangerous to human beings would be reached. To date experimental work indicates that such is not the case.²⁹

Recently studies have been reported on the effect of P^{32} on the biochemical oxygen demand. In their conclusions Grune and Eliassen⁸ state that radioactive phosphorus (P^{32}) when present in concentrations at or below 10 millicuries per liter exerts no significant effect on 1) the reaction velocity constant of BOD, k , 2) the ultimate first-stage BOD value, L , and 3) the 5-day BOD, $y_t = 5$.

Adsorption on sewage sludge was tried and developed at Los Alamos. It is based on the premise that radioactivity does not unfavorably affect biological growth and is accumulated within or on these organisms. Ruchhoft²⁴ has proposed that the activated sludge process be used to adsorb, hold and remove long-lived inorganic radioisotopes during the development and propagation of cultured floc. Laboratory experiments to determine the effect of adding plutonium to activated sludge have been made. An average reduction of about 96 per cent in the alpha count in the treated sewage was reported after 23 hours aeration and one hour settling when the initial concentration was 1.4 micrograms of plutonium per liter of sewage. A tolerance level of 0.001 micrograms of plutonium per liter of sewage was established and could be approached if a two-stage countercurrent flow zoogical floc system was provided.

In discussing the use of activated sludge for the removal of plutonium Newell²¹ states that special safety precautions had to be observed in the handling and disposition of the activated sludge because of the high concentration of radioactive constituents in the sludge. Unfiltered samples showed as high as 28 per cent carry over of the radioactivity by suspended matter in the effluent, which suggests that sand filtration is necessary before discharge of the effluent to assure effectiveness of the process as a whole.

In preliminary studies in which carrier-free I^{131} was added to aerated and stirred activated sludges, removals in excess of 90 per cent have been reported²⁷ following periods of aeration of 24 to 48 hours. About 60 per cent of the radioactive constituents in the evaporator waste slurry were removed by stale activated sludge after 48 hours of stirring.²⁶

Because of the practical difficulties encountered in controlling the foaming due to the presence of large quantities of soaps and detergents in laundry wastes, the use of activated sludge as a method of treating these wastes was ruled out and consideration was given to the use of trickling filters.²² In addition, the volume of waste radioactive sludge produced would be minimal as compared to that produced either by the activated sludge or by a chemical precipitation process. Two-stage laboratory filtration was developed and satisfactory removals were reported with recirculation ratios as high as 15 to 1 when 150 ppm flour, 50 ppm dextrose and 200 ppm of soap and one part of nitrogen and one part of phosphorus to 20 and 80 parts, respectively, of BOD in the waste were added to tap water containing 10 per cent by volume of secondary sludge from the municipal sewerage plant. The raw feed was maintained at 50 ml/min corresponding to 0.3 mgad or about 150 pounds BOD per acre-foot per day on the basis of the primary filter only.

Some features of operation, as indicated by the data in Table 9, are interesting in that in many cases the BOD reduction in the second stage was very small. However, these relatively inconsequential BOD reductions were accompanied by substantial reductions in the plutonium residual of the final effluent. Throughout the study the phosphate feed was kept constant at 15 ppm and the final effluent showed a definite phosphate content. The lowest plutonium residuals were associated with maximum nitrate contents in the effluent. The suspended solids content of the effluent averaged about 10 ppm and filtration through sand would remove the suspended solids and any plutonium affixed to these solids.

The removal of carrier-free I^{131} by low-rate trickling filters has been studied by Carter.⁴ He found that removals of at least 85 per cent could be expected when laboratory filters were dosed with settled sewage

TABLE 9. PLUTONIUM REMOVED FROM LAUNDRY WASTES BY A TWO-STAGE TRICKLING FILTER
Summary of Selected Data for the Period from February 1 to July 10²²

Dur. of Exp.	Obs. Per.	No. of Obs.	Recirculation Pattern ¹					BOD: ppm			Nitrogen						Plutonium c/m/l ²		
			Raw Feed	Pri. to Sec.	Sec. to Pri.	Pri. to Pri.	Sec. to Sec.	Raw	Pri. Eff.	Sec. Eff.	Ammonia ³			Nitrate ⁴					
											Raw	Pri. Eff.	Sec. Eff.	Raw	Pri. Eff.	Sec. Eff.			
2/1 2/24	2/15- 2/24	6	1	6.6	6.6	—	—	335	22	12	0	0	0	0	7	10	731	140	103
2/28 3/20	3/9- 3/20	6	1	—	—	—	12.0	18.0	406	56	18	3	0	0	2	5	450	192	134
3/22- 4/24	4/7- 4/24	7	1	—	—	—	6.4	22.0	380	26	3	10	3	0	16	38	638	145	37
4/24- 6/9	5/1- 6/9	15	1	—	—	—	6.4	22.0	213	9	4	0	0	0	9	16	325	120	80
6/9- 7/10	6/21 7/10	8	1	—	—	—	6.0	6.0	236	7	2	0	0	0	32	38	190	66	46

These data show average BOD removals, nitrogen utilization and results of plutonium assays for the indicated observation periods and recirculation patterns.

(1) Values listed are ratio of volume recirculated to raw feed to primary filter. Recirculation is from bottom of settling tank. Raw feed maintained at 0.3 mgad.

(2) Raw values are on straight wastes. Primary effluent and secondary effluent values are obtained from samples filtered through Whatman No. 2 fluted filter paper.

(3) Direct Nesslerization method.

(4) Phenoldisulfonic method.

(5) Plutonium results are reported in counts per minute per liter. Raw values are on straight wastes. Primary effluent and secondary effluent values are obtained from samples filtered through Whatman No. 2 fluted filter paper.

containing carrier-free I^{131} at a rate of 2 mgad. The writer investigated the effect of higher feed rates (4.1 and 4.45 mgad) and the effect of the addition of carrier-KI on the removal of I^{131} from sewage. At the feed rate of 4.1 to 4.45 mgad a removal of 50 per cent of the carrier-free I^{131} was obtained. The addition of carrier-KI to the I^{131} reduced removals from 50 per cent down to as low as 5 per cent. Earlier studies made by the writer showed that raw sewage would remove from 17 to 27 per cent of the carrier-free I^{131} . These values were corroborated in later studies since it was found that the raw sewage showed estimated removals of approximately 12 to 24 per cent; the addition of carrier-KI reduced the removals by raw sewage to less than 2 per cent.

Metallic Displacement or Scrubbing

Metallic displacement has been used successfully for the recovery of ruthenium and other substances. The effectiveness of such a procedure is illustrated by data obtained with the decontamination unit developed and described by Lauderdale and Emmons¹¹ which included as the first step in the process passage of the contaminated liquid through a bed of steel wool (corresponding to an iron scrub). These results are shown in Table 10.

TABLE 10. RADIOCHEMICAL ANALYSIS OF ACTIVITY ADSORBED BY THE STEEL WOOL IN THE DECONTAMINATOR¹¹

Isotope	Activity c/m/ml	% of Total Activity Removed
Total gross beta	2.35×10^9	85.26
Ru	4.43×10^7	95.96
Zr	1.72×10^8	99.39
Sr	3.19×10^8	69.72
Total rare earths	1.54×10^9	86.81
Ce*	6.81×10^8	97.13
Cs	2.39×10^6	59.74
Nb	6.99×10^6	98.7
Te	1.15×10^7	98.34

*Ce is also included in total rare earths.

Sand Filtration

Although little information is available on the removal of radioactive substances by sand filtration, unpublished communications indicate that many of them are removed by adsorption on sand grains. In the sand filtration of settled effluents containing P^{32} and I^{131} , experience at ORNL shows that the former was removed to an appreciable extent (Table 6), but that there was no measurable removal of the latter. The P^{32} adsorbed could be eluted from the sand grains by acid and alkali washes.

Crystallization

The writer has reported studies²⁷ in which 200 ml samples were frozen, and found that concentration of radioactivity had taken place in the core of the ice cake. Crystallization is not restricted to the separation of solids by freezing alone, but may be applied to many forms of chemical reactions.

Solvent Extraction, Electrolytic Separation, Differential Volatility, and Electrodialysis

No large scale uses of solvent extraction, electrolytic separation, differential volatility, and electrodialysis are known to the writer. These techniques have found wide use as separation processes for isolating and recovering specific radioisotopes from fission products and special irradiations.

Sludge Disposal

All of the methods described above are used to remove radioactivity from the liquid fraction and to concentrate that activity in the solid phase or sludge that is produced (this is not the case with the extraction processes which are used for separations). The disposal of this sludge presents a problem. At present most of the radioactive materials are stored to decrease in activity by decay. In other instances the material is carried out to sea for disposal. The question of discharge of radioisotopes into the oceans has been discussed by Scott²⁵ and the use of concentrated radioactive wastes as liquid for making concrete blocks which may be dumped into the ocean has been noted by Western.³⁰ Some practical difficulties arise in making concrete blocks since certain chemical agents—ammonium nitrate, Calgon and sodium—are reported by E. C. Pitzer to inhibit setting of the concrete.

Where incineration is possible, providing precautions are taken to prevent contamination by volatile gases or fly ash, further concentration or reduction in volume may be obtained. The reduced volume of solid matter then may be placed in suitable containers and buried in controlled areas or stored for decay or for future recovery. In the selection of sites for the burial of any radioactive materials Overstreet²³ recommends that consideration should be given to the following: (1) precise location records, (2) geology of the area, (3) type of storage container used, (4) no dilution with stable isotopes, (5) depth of root zone, (6) type of soil, (7) electrolyte content of the soil, (8) depth, and (9) ground water location and movement.

TABLE 11. MAXIMUM PERMISSIBLE CONCENTRATION UNDER CONSIDERATION FOR CERTAIN RADIOISOTOPES IN WATER AND AIR¹⁸

Element	Half Life*	Microcuries per cc ($\mu\text{c}/\text{cc}$)	
		In Water	In Air
U Nat. (Sol.)	4.50×10^9 years	7×10^{-5}	1.7×10^{-11}
U Nat. (Insol.)	4.50×10^9 years		1.7×10^{-11}
U ²³³ (Sol.)	1.62×10^5 years	1.5×10^{-4}	1×10^{-10}
U ²³³ (Insol.)	1.62×10^5 years		1.6×10^{-11}
Ra ²²⁶	1620 years	4×10^{-8}	8×10^{-12}
Rn ²²²	3.83 days	2×10^{-6}	1×10^{-8}
Pu ²³⁹ (Sol.)	2.41×10^4 years	1.5×10^{-6}	2×10^{-12}
Pu ²³⁹ (Insol.)	2.41×10^4 years		2×10^{-12}
Po ²¹⁰ (Sol.)	138.3 days	3×10^{-5}	2×10^{-10}
Po ²¹⁰ (Insol.)	138.3 days		7×10^{-11}
C ¹⁴ (CO ₂)	5,720 years	3×10^{-3}	1×10^{-6}
H ³	12.5 years	0.2	2×10^{-5}
Ca ⁴⁵	152 days	5×10^{-4}	3×10^{-8}
P ³²	14.3 days	2×10^{-4}	1×10^{-7}
K ⁴²	12.44 hours	1×10^{-2}	2×10^{-6}
S ³⁵	87.1 days	5×10^{-3}	1×10^{-6}
Na ²⁴	14.9 hours	8×10^{-3}	2×10^{-6}
Cl ³⁶	4.4×10^5 years	2×10^{-3}	4×10^{-7}
Fe ⁵⁵	2.91 years	4×10^{-3}	6×10^{-7}
Fe ⁵⁹	46.3 days	1×10^{-4}	1.5×10^{-8}
Mn ⁵⁶	2.59 hours	0.2	3×10^{-6}
Cu ⁶⁴	12.88 hours	8×10^{-2}	6×10^{-6}
I ¹³¹	8.0 days	3×10^{-5}	3×10^{-9}
Sr ⁸⁹	53 days	7×10^{-5}	2×10^{-8}
Sr ⁹⁰ + Y ⁹⁰	25 years	8×10^{-7}	2×10^{-10}
A ⁴¹	1.78 hours	5×10^{-4}	5×10^{-7}
Xe ¹³³	5.271 days	4×10^{-3}	4×10^{-6}
Xe ¹³⁵	15.3 minutes	1×10^{-3}	2×10^{-6}
Co ⁶⁰	5.2 years	2×10^{-2}	1×10^{-6}
Au ¹⁹⁸	2.69 days	3×10^{-3}	1×10^{-7}
Au ¹⁹⁹	3.3 days	7×10^{-3}	2.5×10^{-7}
Cr ⁵¹	26.5 days	0.5	8×10^{-6}
Ni ⁵⁹	$(2-3) \times 10^5$ years	0.25	2×10^{-5}
Mo ⁹⁹	68.3 hours	14	2×10^{-3}

*Half-life values have been added by the writer.

INSTRUMENTATION

Since radioactive elements cannot be determined by the relatively simple physical and chemical procedures usually employed in the sewage and industrial waste field, special electronic or photosensitive instruments are used. One of the instruments used for measuring radioactivity is the Geiger-Mueller end-window counter. Its use in the hands of an experienced technician, who is aware of its limitations, will give fairly reliable results particularly in measuring the activity in liquid wastes

that have a low solids content. A discussion of the evaporation method for liquid waste monitoring was presented recently by Cowan and Nehemias.⁵

Where larger quantities of radioactivity may be encountered it may be necessary to provide suitable instrumentation for environmental and personnel monitoring. These instruments have been described by Morgan.²⁰

HEALTH HAZARDS AND POLLUTIONAL EFFECTS

Radioactive wastes may be hazardous in two ways: (1) chemical toxicity and (2) radioactivity. During the past few years certain chemicals have been produced in macro quantities where once they were merely laboratory curiosities. As a result, in some instances, some of the rarer elements may be toxic and little or no information is available concerning their toxicity. Radioactive substances are hazardous substances and continuous exposure to them may be harmful. To evaluate the hazard, health physicists have established maximum permissible concentrations (MPC) for specific radioisotopes in water and air. The procedures for computing these tolerances have been reported by Morgan.¹⁹ The latest MPC values under consideration by the Sub-committee on Internal Dose of the National Radiation Protection Committee are given in Table 11.¹⁸

References

1. Ayres, J. A., AECD-2802. U.S. Atomic Energy Commission (December 7, 1949).
2. Browder, F. N., *Ind. Eng. Chem.*, **43**, 1502 (1951).
3. Butrico, F. A., Mass. Inst. of Tech. NP-1623. U.S. Atomic Energy Commission, Tech. Inf. Div., Oak Ridge, Tenn. (May 19, 1950).
4. Carter, M. W., Masters Thesis Investigations at Oak Ridge National Laboratory, Georgia Institute of Technology (1950).
5. Cowan, F. P., and Nehemias, J. V., *Nucleonics*, **7**, 5, 39 (1950).
6. Ginell, W. S., and Hatch, L. P., Brookhaven National Laboratory (June 1950).
7. Gorman, A. E., *Jour., New England Water Works Assoc.*, **64**, 148 (1950).
8. Grune, W. N., and Eliassen, R., *Sew. and Ind. Wastes*, **23**, 141 (1951).
9. Horn, F. L., BNL-58 (C-11). Brookhaven National Laboratory (June 1950).
10. Jacobson, L., and Overstreet, R., MDDC-1006. U.S. Atomic Energy Commission Oak Ridge, Tenn.
11. Lauderdale, R. A., and Emmons, A. H., *Nucleonics*, **8**, 21 (1951).
12. Lauderdale, R. A., *Ind. Eng. Chem.*, **43**, 1538 (1951).
13. Levy, H. A., *Chem. Engr. News*, **24**, 3168 (1946).
14. Los Alamos Scientific Laboratory. The Effects of Atomic Weapons, Chapter VIII, Supt. of Documents, U.S. Govt. Printing Office, Washington 25, D.C. (Sept. 1950).
15. Love, S. K., *Ind. Eng. Chem.*, **43**, 1541 (1951).

16. MacKintosh, A. D., *Nucleonics*, **5**, 5, 48 (1949).
17. McCullough, G. E., *Ind. Eng. Chem.*, **43**, 1505 (1951).
18. Morgan, K. Z., Chairman. Letter of January 23, 1951, to Members of the Subcommittee on Permissible Internal Dose. Minutes of Meeting of the Subcommittee on Internal Dose of the National Committee on Radiation Protection. See also Maximum Permissible Amounts of Radioisotopes in the Human Body and Maximum Permissible Concentrations in Air and Water. Natl. Bur. Standards. U.S. Dept. of Commerce, *Handbook 52*, (March 20, 1953).
19. Morgan, K. Z., *J. Phys. Colloid Chem.*, **51**, 984 (1947).
20. ———, Supplement to U.S. Nav. Bull., p. 142 (March-April 1948); *Proc. Inst. Radio Engrs.*, **37**, 74 (1949); *J. Ind. Hyg. Toxicol.*, **30**, 286 (1948).
21. Newell, J. F., AECD-2712 (Oct. 4, 1949).
22. Newell, J. F., Christenson, C. W., Krieger, H. L., Moeller, D. W., Mathews, E. R., and Ruchhoft, C. C., *Ind. Eng. Chem.*, **43**, 1516 (1951).
23. Overstreet, R., Recommendations Pertaining to the Burial of Radioactive Wastes in Soil. Private Communication.
24. Ruchhoft, C. C., *Sewage Works J.*, **21**, 5, 877 (1949).
25. Scott, K. G., *Nucleonics*, **6**, 1, 18 (1950).
26. Straub, C. P., Presented at the 117th Meeting of the Am. Assoc. for the Advancement of Science, Cleveland, Ohio. (Dec. 26-30, 1950.)
27. ———, *Sewage and Ind. Wastes*, **23**, 188 (1951).
28. Symposium on Radiochemistry Laboratories. *Ind. Eng. Chem.*, **41**, 227-250 (1949).
29. Warren, S. Digest of Proceedings, Seminar on the Disposal of Radioactive Wastes Sponsored by the U.S. Atomic Energy Commission, Washington, D.C. (January 24-25, 1949).
30. Western, F., *Nucleonics*, **3**, 2, 43 (1948).

17. Miscellaneous Wastes

Willem Rudolfs

Department of Sanitation, Rutgers University, New Brunswick, N.J.

In addition to the waste problems discussed in the various chapters there are a number of manufacturing processes producing wastes which are important locally, or wastes which are widely discharged in comparatively small quantities, or those which are frequently discharged into municipal sewers causing increased loading or difficulties at sewage treatment plants.

LAUNDRY WASTES

One of the most common liquid wastes discharged is laundry waste. As a rule the waste is discharged into municipal sewers. Larger volumes of soapy wastes from power laundries, scouring establishments and plants employing soap solutions may require pretreatment before discharge into municipal sewers or must be treated separately.

Soapy solutions have high oxygen demands; pure soaps require almost twice their weight in oxygen for satisfaction of the 5-day BOD and commercial varieties of soap about $1\frac{1}{2}$ times.

TABLE 1. AVERAGE ANALYSES OF COMMERCIAL AND DOMESTIC LAUNDRY WASTES

	Commercial	Domestic
pH	10.3	8.1
Total alkalinity (ppm)	511	678
Total solids (ppm)	2,114	3,314
Volatile solids (ppm)	1,538	2,515
BOD, 5-day, (ppm)	1,860	3,813
Oxygen consumed (ppm)	868	1,045
Grease (ppm)	554	1,406

The volume of laundry waste normally is 5 to 10 per cent of the average daily flow of sewage, but the waste is from 10 to 20 times stronger.⁹ Average analyses of domestic and commercial laundry waste are shown in Table 1, but laundry practice varies and both stronger and weaker wastes are frequently observed.³¹

Separate treatments for clarification by means of chemicals have included lime, alumino-ferric, calcium chloride, iron salts, alum and salt (sea) water. Treatment with alum and acid has been claimed to be less costly than ferric sulfate-lime or acid-lime treatment,³ but purification results comparable to acid-alum treatment with ferric sulfate and lime at about equal cost have been reported.³² It appears that adjustment of pH to 6.4 to 6.6 with acid prior to coagulant addition produces optimum purification at lowest cost.^{2,21} The use of carbon dioxide to lower alkalinity and the pH value prior to coagulation has produced excellent results.^{15,35}

The oxidation of laundry waste can be successfully accomplished on trickling filters, handling rates of application of 1.5 mgad despite grease loadings up to 490 pounds per acre foot per day, pH values of 11.0 and alkalinities of 1,000 ppm in the raw waste.²¹

Activated sludge oxidation of laundry waste is feasible, but longer periods of aeration than commonly used for sewage are required.³⁸

One difficulty seldom mentioned, but frequently encountered in treating the waste with chemicals, is settling. The release of carbon dioxide on treatment causes partial flotation of the sludge. Experiments on treatment with flotation by vacuum⁸ produced better results than settling. Treatment of waste waters after equalization reduces the chemical demand and aids in clarification. Pre-aeration or flocculation prior to settling aids removal of impurities.⁹ Gehm⁹ summarized our knowledge of laundry waste treatment by the following statements:

(1) "To remove about 75 per cent of oxygen consumed, solids, and grease, laundry waste can be treated most economically by acidification with H_2SO_4 , CO_2 , or SO_2 , followed by coagulation with alum or ferric sulfate. It can also be coagulated partly and completely by many salts and acids and by lime, but in most cases such treatment is too costly.

(2) Laundry waste can be purified to a high degree by means of conventional and probably high-rate trickling filter, or by the activated sludge process if long aeration periods are used.

(3) The sludge obtained can be dried on sand beds directly or very probably digested anaerobically, or filter pressed. Final disposition of undigested sludge can be accomplished by a soap recovery process or by incineration.

(4) Waste treated by chemical coagulation can be further purified by passage through a biological filter or by the activated sludge process.

(5) Sewage containing any percentage of laundry waste can be treated on a biological filter of adequate capacity and correctly designed for this purpose.

(6) The activated sludge process employing normal aeration periods

can handle sewage containing laundry waste in concentrations approaching 20 per cent."

BEET SUGAR

Manufacture

Beet sugar production in 85 plants operating in 16 states amounted to 1,369,000 tons in 1948, representing 12.34 per cent of the world total.¹⁶ The liquid waste produced from 9,422,000 tons of beets processed is highly polluttional, estimated to have a population equivalent of 17,000,000, based upon the BOD of the wastes. The polluttional problem is enhanced, because beet sugar manufacture is seasonal, lasting from 60 to 100 days, and the largest production is restricted to only 3 states, California, Colorado and Idaho.

In standard beet sugar manufacture, the beets are dug, topped by machine and by hand, transported to railroad or storage areas, from which they are conveyed by means of water in flumes to the plant. Transportation by water removes most of the sand, soil, floating debris and leaves. The beets are discharged from the flume to a beet wheel, the water discharged or recirculated, and the beets elevated to vat type rectangular chambers, equipped with agitators, for washing. Final wash sprays may be employed and the washed beets passed over a picking table for removal of spoiled beets and foreign material. The washer water is frequently passed through coarse screens to recover pieces of beets and roots for stock food. The washed beets are weighed, sliced into long narrow V-shaped ribbons, called "cossettes," and the cossettes conveyed to diffusers for sugar extraction.

The factories operate either on what is known as the "straight house" in which sugar is extracted to the point at which heavy molasses is obtained, or with the addition of the Steffens house, in which additional sugar is obtained from the molasses.

A flow sheet, Figure 1, shows the general operations and sources of wastes.

Battery diffusers, vertical, cylindrical, steel tanks holding from 3 to 7 tons of cossettes and employing the counterflow principle, are dumped in rotation. Fresh water enters the cell containing cossettes which have been longest in the system; the water then passes progressively through cells which have been under diffusion shorter periods of time and leaves the battery after passing through the cell which has been most recently filled with cossettes.

The pulp is screened (drained), pressed and sent to the pulp dryers, or after screening put into silos.

The raw juice from the diffusion battery is heated and discharged into the first carbonation tank where it is treated with milk of lime and carbon dioxide bubbled through the limed juice. The precipitate is filtered or settled and the juice is carbonated a second time, again filtered, and then treated with SO_2 gas and filtered a third time. The sludge and material retained on the filters, called "lime cake," is diluted and discharged as a slurry.

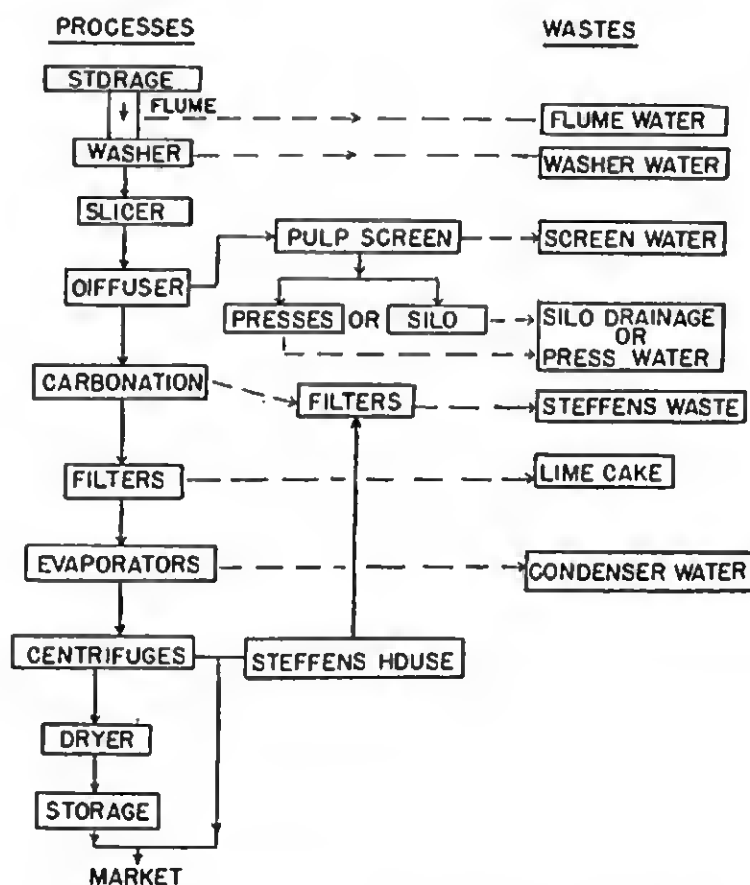


FIGURE 1. Simplified beet-sugar factory flow diagram

The juice is concentrated in multiple-effect evaporators, again filtered and the sugar recovered by evaporation in vacuum pans until crystals of the desired size are obtained. The sugar crystals are separated from the liquid in centrifugals. The residue, "beet molasses," is either sold or further treated for sugar recovery by the Steffens process.

The Steffens process consists of diluting the molasses to a specific concentration and treating with a sufficient amount of lime to produce a calcium saccharate, which is removed from the liquor by filtration and the sugar recovered by treating with CO_2 .

Recent developments of organic and resinous types of ion exchangers²⁰

makes it possible to increase the efficiency of removal of non-sugars from second carbonation beet juice prior to evaporation and crystallization, resulting in increased sugar yield, less molasses production, and a molasses that can be converted by further ion exchange treatment into an edible product. The cation exchangers are regenerated with H_2SO_4 solutions, and the anion resins are regenerated by washing with an alkali solution composed of NaOH and ammonia. In 1951, there were 3 sugar refineries known to use ion exchange for treatment of all or part of the sugar beet juices.¹⁶

Volume and Character of Wastes

There is considerable variation in flow and characteristics of the wastes produced from different factories. Flows and analytical results "considered to be representative"¹⁶ are shown in Table 2. Flume water and condenser water are the largest volumes but have the lowest BOD values.

TABLE 2. CHARACTERISTICS AND VOLUMES OF WASTES¹¹

Waste	Flow/Ton Beets (Gals)	BOD (ppm)	Susp. Solids (ppm)	BOD/Ton Beets Sliced (lbs)
Flume water	2,600	210	800-1,300	4.5
Screen water				
(a) bottom dump cell	240	980	530	2.0
(b) side dump cell	1,420	500	620	5.9
(c) continuous	400	910	1,020	3.0
Silo drainage	210	7,000	270	12.3
Press water	180	1,710	420	2.6
Steffens waste	2,640*	10,500	100-700	231†
Lime cake slurry	90	8,600	120,000	6.5
Lime cake lagoon eff.	75	1,420	450	0.89
Condenser water	2,000	40		0.67

*per ton of molasses processed on a 50 per cent sugar basis.

†per ton of molasses washed (including foreign molasses).

With the exception of condenser water, the flume water is roughly 70 per cent of the total waste. This waste contains varying amounts of tops and roots, leaves, stones, sand, silt and other materials in suspension, hence considerable variation in total suspended solids occurs.

The process water, smaller in volume than flume water, has a higher BOD and varying amounts of suspended solids, much of which is organic in nature. It contains a comparatively large amount of sugar and other organic material in solution.

The concentration of the waste is affected by the type of diffuser, efficiency of pulp screen, and operation of the presses.

Lime cake from the filters amounts to about 200 pounds per ton of

beets processed. The amount of water added, depending to a certain extent upon the type of filter and the operator, determines the volume and strength of the lime slurry. The cake is mainly composed of CaCO_3 and organic and inorganic impurities removed from the juices. It settles readily in a short period of sedimentation in the lime pounds and has a pH value of about 11.7.

The pulp silo drainage from wet pulp storage in open silos varies with the quantity of pulp stored, efficiency of the pulp screen, fermentation, and rainfall. Organic acids production during decomposition result in pH values of about 4.0. The silo drainage continues after plant operation ceases and may become stronger if the pulp remains in the silo until warm weather.

The Steffens house waste is the strongest and is estimated to constitute about 50 per cent of the total factory wastes. Approximately 2,640 gals of waste are produced per ton of molasses washed.¹⁶ It contains from 2.5 to 4 per cent total solids, nearly all of which are in solution. The pH may be as high as 12.6.

No specific information is available concerning the volume and characteristics of the acid and alkaline wastes from regeneration of ion exchange resins. It is postulated that the pollution load from ion exchange treatment of second-carbonation juice should resemble the waste from a Steffens plant more closely than from a straight house.

Waste Reduction

As in practically all industrial processes beet sugar waste can be reduced by good housekeeping methods, including modification of equipment or minor process changes, by segregation and reuse, or by-products recovery.

Waste from the pulp screen can be eliminated by the continuous diffuser and a mechanical conveyor to transport the drained pulp from the diffuser to the presses. Lime cake drainage can be eliminated by transporting the cake from the factory in a fairly dry condition from the presses to the filters. Reburning and defecation of lime cake, practiced at some plants, encourages handling of dry cake. Pulp silo drainage from storage of wet pulp in open pits can be eliminated by pressing and drying of the pulp. Recirculation of flume water, practiced at a number of plants, preferably with use of short time detention basins to remove the settleable solids, reduces the volume of waste materially. Odors developing from the recirculated water appear to be effectively controlled by intermittent chlorination.²⁵ It is common practice to reuse condenser water or condensates for fluming and washing beets, for diffusion battery water, for washing lime cake, for dilution of lime cake, for cleaning filters, and for boiler feed. At some beet sugar factories in

England the condenser water is reused in the condensers. Growth of bacteria and fungi in cooling towers is controlled by chlorine treatment.³⁶

Treatment

Methods of treatment vary considerably in detail and accomplishments, but practice, in general, is confined to reuse of some waste for fluming and ponding and settling devices for removal of settleable solids.

Ponding and Irrigation

Ponding of the large volumes of flume water (about $\frac{3}{4}$ of the entire waste volume) in settling ponds of the flow through type is usually given first consideration, but decomposition of the accumulated organic solids soon give rise to gas production, H_2S odors, and flotation of solids, with the result that the pollution characteristics of the effluent may be worse than the raw wastes. The usual hazard of leaks and breaks of the earthen embankments is always present, allowing the concentrated wastes to escape.

Ponding of lime slurry in units of sufficient size to retain the sludge during the campaign with draw off of the supernatant liquor to the stream at high river flows has been successful, provided the accumulated lime sludge is removed annually. The lime sludge is used by farmers for soil conditioning.

Steffens waste ponding has been a rather general practice in the past, but the high BOD of the material requires that it is held for long times and can be discharged only when sufficient oxygen is available in the receiving stream, hence careful control is necessary.

Undoubtedly, long time ponding can be made into an effective method of treatment. Some information on the degree of purification is available,²⁸ but proper technic and efficient operation must be worked out.

Screens, Grit Chambers, Settling

Clarification of flume and process water by means of a drag or preferably rotary type, followed by parallel grit chambers similar to those used in sewage treatment processes, and conventional types of settling tanks^{5,6} results in about 90 per cent suspended solids and 40 per cent BOD reduction from flume water, about 93 per cent of suspended solids and 47 per cent BOD from straight house process water, and over 90 per cent suspended solids and over 60 per cent BOD from Steffens waste.

Coagulation

A coagulation tank may be an integral part of the settling tank or a separate unit. Coagulation for 20 to 30 minutes with the aid of lime increases the efficiency of the settling tanks. Coagulation of flume water

improves removal of suspended matter and some additional BOD, but the additional cost may not always be justified by the results.

Biological Filtration

Biological purification of settled flume water, pulp water, and diluted Steffens waste is feasible,¹⁷ but because it takes from 2 to 3 weeks to develop an active film on the filter media, the short campaign and the season of the campaign, biological treatment of the wastes is not generally practiced and said to be not very efficient.²² Large scale experiments³⁶ with effluent from ponds placed on trickling filters 12 feet in diameter and graded medium of 1 to 1.5 inches, and applying 300 gal/cu yd a day produced effluents as low as 5 ppm BOD.

Sludge Treatment

The usual method of ponding lime slurry is unsatisfactory in many cases because of the drainage or run off reaching streams. The ponds rapidly fill to capacity and require frequent cleaning to maintain maximum efficiency of suspended solids removal. Concentrated lime slurry can be vacuum filtered at a rate of about 100 gals per square foot of filter area per 24 hrs.⁶

Flume water and process water sludge produced during a campaign can be ponded, requiring a pond capacity of about 1.1 acres, 6 ft deep, per 1,000 tons beets a day processed during a 100 days' campaign. On a 1,000 ton per day basis, the estimated dry sludge produced is about 10.2 tons a day, exclusive of grit removed by the grit chambers.

Vacuum filtration is considered the most satisfactory method of handling sludge from the flume and process water. The flume water sludge requires preconditioning with lime, varying from 50 to 80 pounds of lime per 1,000 gals of sludge, producing a cake of 45 to 50 per cent moisture.

Process water that has been coagulated with lime does not require preconditioning.⁶ The moisture content of the filter cake is about 50 to 55 per cent with an average rate of filtration of 100 gals of sludge per square foot per 24 hrs.

CANE SUGAR

Sugar cane with a satisfactory sugar content is cut, the stalks squeezed in rotary extractors and the juice evaporated, purified, crystallized and molasses separated. The cane residue is dried and frequently burned for steam production. Sulfur is added to produce a white product and lime is used for pH control. The blackstrap molasses can be converted into alcohol and numerous other by-products. The water

used in the various processes averages about 500 gals per ton of sugar cane processed.

The waste water originates mainly from the purification and crystallization processes, molasses and its by-products, and condenser water. The BOD and suspended solids content of mill effluents vary, depending upon the volume of water used, the efficiency of operation, and the extent and type of by-products recovery.

The pollutional characteristics of the combined mill wastes vary from 250 to 1,200 ppm BOD and 150 to 2,300 ppm suspended solids.

Disposal of waste is frequently by discharge into streams and methods of treatment are in its infancy. Stone³⁷ believes that all waste products should be reused as sources of fuel, fertilizer, by-products, or irrigation water.

SUGARY WASTES

In the process of manufacturing candied fruit and similar products, large quantities of sugar may be discharged mixed with other preserving agents. Raw wastes produced contain from 16,000 to 18,000 ppm total solids, of which about 75 per cent are volatile in a soluble state, from 200 to 450 ppm suspended solids, and from 9,000 to 95,000 ppm reducing sugars. The average BOD of over 100 samples showed it to be 7,500 ppm. In addition, the raw waste contains sulfur dioxide in varying amounts.

Laboratory and pilot plant experiments dealing with digestion and trickling filters showed that a high degree of purification could be obtained, but that after a number of months, operation deterioration of the effluent occurred, probably because of the toxic preservatives present.

Results obtained with high-rate trickling filters, operated in series and in parallel over a period of several years with domestic sewage and candied fruit waste having average BOD values of 540 to 630 ppm, show that purification is feasible to a high degree. It appears that the efficiency of double filtration (series) is about 2.5 to 3 times as high as that of single (parallel) filtration when equal loadings are used.

RUBBER

There are, in general, three sources of rubber wastes: (1) manufacture of rubber commodities, (2) rubber reclaiming, and (3) synthetic rubber.

Commodities

The manufacture of commodities is essentially a washing, compounding, calendering and curing process, followed by the manufacturing of

many kinds of rubber products. The waste produced consists essentially of impurities removed by washing from the crude rubber and large volumes of cooling water.

Reclaiming

The recovery of used rubber is accomplished by shredding old rubber, removal of iron and sometimes recovery of part of the cotton fabric. In general, the ground rubber and fabric are subjected to a caustic treatment under high temperatures to destroy the fabric. The rubber is then washed, dried, milled, strained and refined.

The discharge from a reclaiming plant, including process waste, sewage and wash water¹ are given on the basis of samples taken over a period of several month as:

	Av.	Max.
Total solids (ppm)	49,280	173,820
Suspended solids (ppm)	15,550	77,340
BOD (ppm)	1,490	7,800

The waste frequently contains considerable hydroxide alkalinity with pH values varying from 10.9 to 12.2.³³ The waste is treated at the plants in settling devices for recovery of settleable material. The sludge is vacuum filtered, dried and used. The effluent is discharged into municipal sewers or in some instances directly into receiving waters. The causticity of the waste together with the great variation in strength and volume may interfere with municipal biological treatment devices. Neutralization by exhaust or flue gases aids in the treatment.

Synthetic

The chemical, petroleum and rubber industries in the United States made only a moderate effort to develop synthetic rubber prior to 1940. During the war the synthetic rubber production reached over 1,000,000 tons requiring the construction of 53 plants of various types,¹³ including copolymer units, styrene plants, butadiene plants utilizing alcohol and petroleum for feedstocks and butylene feedstock units, as well as necessary catalysts, chemical and solvent operations.

Crude synthetic rubber is produced in two steps: (1) production of raw materials for polymerization, and (2) the actual polymerization operation.²⁹ The principal raw materials for polymerization, in the production of butadiene polymers and copolymers, consist of butadiene, styrene, and acrylonitrile. Butadiene and styrene were the most important of the raw materials used.

The pollutional characteristics and approximate daily discharges are

shown in Table 3. The wastes are objectionable because of the high BOD and odor and taste imparting properties. The large volume of waste from the main sewer has a population equivalent of 474,000 and

TABLE 3. ANALYSES OF TYPICAL WASTES FROM SYNTHETIC RUBBER²⁵

Plant	Flow (mgd)	pH	Solids (ppm)	Susp. Solids (ppm)	BOD (ppm)	Odor Conc.
Butadiene	1.90	2.8	300	28	2,550	16,100
Styrene	4.62	6.2	150	4	180	690
Copolymer plant:						
Process waste	2.34	4.3	5,580	12	69	62
Recovery and reactor	0.39	8.0	570	24	492	8,700
Main sewer*	2.63	7.0	6,530	46	168	930
Main outfall†	119.4	5.4	270	15	81	460

*Process, recovery and reactor waste mixture.

†Butadiene and styrene waste plus large volume of condenser water.

intense odor producing property, which is noticeable in very low concentrations. The odors are not removed from solution at the same rate as BOD and the normal self purification occurring in streams is of little assistance in removing odors.

The waste has been treated by neutralization, regional separators, final separators, settling tanks and hay-filters¹³ primarily for removal of oil and suspended materials. Actual purification as far as BOD removal is concerned, is small.

A considerable amount of experimental work to remove the taste and odor producing substances has been reported,²⁶ including aeration, ehlorination, Na_2SO_3 and Na_2S treatment, and activated sludge, with very moderate success. Investigations to determine methods of reducing the BOD simultaneously with odor removal, show that the wastes are not necessarily toxic to a biological system such as activated sludge, but that separate treatment will fail because of lack of nitrogen and phosphorus and possibly other mineral constituents.²⁶ Compositied wastes could be treated by trickling filters and activated sludge, provided the wastes were mixed with equal volumes of domestic sewage. Experimental results indicate that a biological floc can be developed with smaller volumes of sewage reducing the BOD of the composite waste 60 to 95 per cent and the odor in the effluents to 4 to 8.

GUM WASTES

Before natural gums are used in the manufacture of chewing gum, they must be cleaned of all sand, dirt, debris and other undesirable material found in the gum as received from its sources. A wide variety

of natural gums from the tropical rain forests of the world are utilized, compounded according to various formulas, thoroughly dry-mixed, steam-cooked and washed several times in hot detergent solutions. The cleansed gum is further processed before shipment to the chewing gum manufacturer.

The wastes are discharged at a temperature of about 140°F, have a deep red color, contain pieces of gum and considerable amounts of soluble organic material in addition to the sand, dirt and debris. Most of the coarse suspended material settles readily in 30 to 60 minutes and is not a particular problem of disposal other than removing and disposing of the accumulated material.

A typical analysis of the gum wastes¹⁸ is as follows:

Total solids (ppm)	13,760
Ash of total solids (%)	33.9
Suspended solids (ppm)	970
Ash of susp. sol. (%)	32.0
Total alkalinity (ppm)	1,800
Total nitrogen (ppm)	220
BOD, 5-day, (ppm)	3,800
pH	10.5

There is considerable variation in the strength of the wastes produced because of the separate washings of the raw gum.

Laboratory results on the treatment of the waste showed that chemical treatment was ineffective, but primary treatment by anaerobic digestion or aerobic sludge treatment was feasible. Anaerobic treatment was easier to control, more uniform, more stable, and required simpler equipment than aerobic sludge treatment. Secondary treatment of the digester effluent by trickling filters and sand filters, followed by chlorination for color removal produced a very high degree of purification.

On the basis of laboratory and pilot plant experiments, a full scale plant, consisting essentially of two continuous upflow digesters, settling tank, trickling filter with recirculation, two sand filters and final settling tank was constructed.²⁴ The plant handles the domestic sewage from the plant in addition to the process waste. Average operation results for a period of 8 months show a flow of about 25,000 gals a day with an over-all BOD reduction of 90 per cent.

DRUM AND TANK CAR CLEANING

There are a considerable number of comparatively small establishments which drain and clean drums, carboys and other containers to be reused. The drums usually contain a variety of relatively small quantities of acids, alkalies, solvents, oils, organic chemicals, petroleum prod-

ucts, etc. Discharge into sewers may cause corrosion, explosion hazards, and interference with biological treatment processes on account of the toxic character of some of the materials.

Treatment of these wastes is usually limited to equalization, settling, and skimming, and aeration to remove some of the volatile substances.

The problem of disposal of waste resulting from tank car cleaning by industries and particularly by transportation companies involves the construction of specialized treatment devices. The General American Transportation Corporation owns and operates over 38,000 tank cars used to ship hundreds of various commodities, among which are petroleum products, coal and wood tar derivatives, synthetic organic chemicals, organic solvents, liquefied gases, inorganic chemicals, food products, and a variety of other materials.¹¹ Cleaning of the empty tank cars is done in 23 maintenance shops distributed over the country, generally involving draining, rinsing, steaming, and sometimes hot caustic spraying. Several specialized methods have been developed in addition to utilization of standard methods of oil separation, equalization mixing and chemical treatment, and settling.

A specialized and novel method of treatment¹¹ consists of adjusting the underflow from mechanical oil separators with H_2SO_4 to pH 4 to 5, mixing the liquid with pulverized coal and feeding the mixture to a series of turbo-floaters. A foaming agent is added. The coal concentrate is thickened, the slurry filtered, the cake mixed with dry coal and burned. The flotation tailings, together with the neutralized effluent are aerated to modify or remove residual aromatic compounds and reduce the BOD. The effluent may be clarified for reuse, ponded or discharged to the receiving water depending upon local conditions.

The diversity of the waste products requires some degree of segregation; alkalies are separated and may be ponded or evaporated, and acid wastes treated with lime. Use of coagulating chemicals is sometimes necessary.

CUTTING AND GRINDING OIL

The different "soluble" oils used for cutting, nut tapping, and grinding present a waste treatment problem, although the quantities may be small. In general, soluble oils are homogeneous compositions containing mineral oil, pine oil, or other hydrocarbon oils; emulsifying agents such as soaps or sulfonated oils, and certain amounts of water.⁷ The BOD values of the oil emulsions vary from 1,300 to 12,100 ppm; the emulsions are usually alkaline.

Laboratory studies on the breaking of the oil-in-water emulsions to recover the major portion of the oil and find methods of treating the

residual liquid showed that CaCl_2 could remove 98 to 99 per cent of the oil and reduce the BOD from 80 to over 97 per cent, depending upon the type of soluble oil used.

Other laboratory studies¹² showed that, for a given soluble oil, the higher the oil content of the emulsion, the easier it was to break the emulsion. A number of different electrolytes will partially or completely break emulsions of several different soluble oils, but not all. The quantity of electrolyte required is frequently so great that it might result in effluents toxic to aquatic life. In general, the effluent will still contain an oil content of 200 ppm or more.

CHICKEN PACKING

A chicken dressing or packing plant is a mechanized slaughterhouse in which the chickens are killed, bled, picked, cleaned, singed, washed, chilled and frozen for shipment. Cleaned but not eviscerated chickens are known as "New York dressed," while the "full pack" includes the removal of entrails and internal washing.^{14,27}

The wastes are derived from: (1) feeder or receiving stations, consisting of manure and spilled food dropped and washed from the floor, (2) battery washing, with or without previous scraping, (3) killing room, containing blood and dirt, some feathers and wax, (4) packing room, consisting mainly of floor washings.

The flow of waste per ton of live chicken processed varies from 1,000 to 3,000 gals. Packing room wastes contribute as much flow as the wastes produced from battery washing and feeder stations.

The strength of the waste in terms of suspended solids and BOD varies greatly, depending upon whether or not the batteries are scraped, how much blood is saved, and good housekeeping. The suspended solids may vary from 500 to 15,000 ppm and the BOD from 300 to 7,500 ppm. The population equivalent on a BOD basis may vary from 30 to 600 per ton of live chickens processed.

Removal of manure from the wire baskets by scraping, use of screens to catch feathers and wax, and saving of blood from the killing room reduce the strength of the waste from $\frac{1}{3}$ to $\frac{1}{2}$.

Treatment by plain sedimentation will remove from 60 to 65 per cent of the suspended solids if the manure from the batteries is removed prior to settling. The sludge can be digested and the clarified effluent subjected to conventional secondary treatment of trickling filters and sand filtration.

DETERGENTS

The production of surface-active agents has been increasing rapidly in the United States from about 28,000,000 pounds of 100 per cent

active material in 1941 to about 1,000,000,000 pounds in 1950. The increasing use of synthetic detergents in homes and industry has raised many questions concerning their effect on sewage treatment processes and streams.

Detergents, a class of surface-active substances used as cleansing agents, can be grouped into anionic, cationic and non-ionic agents. The synthetic detergents are effective under a wide range of pH and do not form insoluble precipitates with water hardness as do many soaps.

In addition to household use, specific uses for surface-active agents in textile, cosmetic, pharmaceutical, metal, paint, leather, paper, and rubber industries is rapidly expanding, because these compounds have properties of dispersing, wetting, and emulsifying.²³

Although great concern has been expressed of the effect of synthetic detergents on sewage treatment devices, it appears that the effects are limited. The replacement of soap by detergents reduces the strength of sewage. The more widely used anionic and non-ionic types of detergents in concentrations found in sewage do not materially interfere with sewage oxidation, whereas the cationic type used for specialized purposes retards oxidation of sewage. Sedimentation of sewage is somewhat impaired, placing a greater load on secondary units. A considerable nuisance may be created in activated sludge processes because of extensive foaming and some adverse effect on the effluent by suspended solids carry-over. Some diminished gas yields from anaerobic digestion units can be expected, but no retardation or inhibition of the processes. There is some interference with chemical coagulation. Anionic and non-ionic detergents have no marked effect on the numbers of coliform organisms in the effluents, but cationic agents cause a considerable decrease in numbers of organisms. Detergents aid somewhat the dewatering of fresh sewage solids.^{4,10,19,30,34}

OTHER

There are many other wastes produced and discharged from various types of industries—to mention only a few widely varying types such as coffee, glue and gelatine, formaldehyde, fish canning, sweet potato starch, fertilizer production, and inert wastes such as phosphates and sand washing. It is, however, impractical and often unnecessary to describe all types of wastes and their methods of disposal, because a number of the wastes can be treated by standard or somewhat modified methods in use for similar types of wastes.

References

1. Barton, E., *Sewage Works J.*, **17**, 501 (1945).
2. Bayer, A., *Texas Eng. Expt. Sta. Bull.*, **42** (1933).

3. Daniels, F. E., *Public Works*, **54**, 190 (1923).
4. Degens, P. N., Van Der Zee, H., Kommer and Kamphuis, Jr., *Inst. Sew. Purif.*, Part 3, 359 (1919).
5. Eldridge, E. F., *Mich. Eng. Expt. Sta. Bull.*, **51** (1933); **60** (1934); **67** and **71** (1936); **78** (1938).
6. ———, "Industrial Waste Practice," pp. 84-114 (1912).
7. Eldridge, E. F., and Purdy, R. W., *Sewage & Ind. Wastes*, **20**, 849 (1918).
8. Eliassen and Schullhoff, *Water Works & Sewage*, **90**, 418 (1943).
9. Gehm, H. W., *Sewage Works J.*, **16**, 571 (1944).
10. Goldthorpe, H. H., and Nixon, J., *J. Inst. Sewage Purif.*, Part I, 109 (1918).
11. Gutzeit, G., *Sewage & Ind. Wastes*, **21**, 91 (1949).
12. Haseltine, T. R., *Sewage & Ind. Wastes*, **21**, 859 (1919).
13. Hebbard, G. M., Powell, S. T., and Rostenbaeh, R. E., *Ind. Eng. Chem.*, **39**, 589 (1947).
14. Heukelekian, H., Orford, H. E., and Cherry, J. L., *Sewage & Ind. Wastes*, **22**, 521 (1950).
15. Hood, J. W., *Proc. N. J., Sewage Works Assoc.*, p. 31 (1941).
16. "Industrial Waste Guide to the Beet Sugar Industry," U.S.P.H.S., Dec. 1950.
17. Levine, M., *Am. J. Pub. Health*, **23**, 585 (1933).
18. Logan, R. P., and Rudolfs, W., *Ind. Eng. Chem.*, **39**, 1673 (1947).
19. Lumb, C., and Barnes, J. P., *J. Inst. Sewage Purif.*, Part I, 102 (1910).
20. Maudru, J. E., *Ind. Eng. Chem.*, **43**, 615 (1951).
21. McCarthy, J., *Public Works*, **73**, 13 (1942).
22. McDill, B., *Ind. Eng. Chem.*, **39**, 657 (1947).
23. Niven, W. W., "Fundamentals of Detergency," New York, Reinhold Publishing Corp. (1950).
24. Orford, H. E., *Sewage and Ind. Wastes*, **23**, 313 (1951).
25. Pearson, E. A., and Sawyer, C. N., *Chem. Eng. Progress*, **46**, 380 (1950).
26. Placak, O. R., and Ruchhoft, E. C., *Sewage Works J.*, **18**, 1169 (1946).
27. Porges, R., *Sewage & Ind. Wastes*, **22**, 531 (1950).
28. Rogers, T. H., *Rept. Tech. Comm. Upper Miss. Bd. of Sanit. Eng.*, Feb. 5, 1947.
29. Ruchhoft, C. C., Placak, O. R., and DeMartini, F. E., *Civil Eng.*, **17**, No. 2, 59 (1947).
30. Rudolfs, W., Manganelli, R., and Gellman, I., *Sewage Works J.*, **21**, 605 (1919).
31. Rudolfs, W., and Setter, L. L., *N. J. Agr. Exp. Sta. Bull.* **610** (1936).
32. Sakers, L. E., and Zimmerman, F. M., *Sewage Works J.*, **1**, 79 (1928).
33. Schaetzle, T. C., *Sewage Works J.*, **17**, 497 (1915).
34. Seriver, A., Jr., *Inst. Sewage Purif.*, Part 3, 351 (1919).
35. Singleton, P., U.S. Pat. 2,196,180 (1910).
36. Southgate, B. A., "Treatment and Disposal of Industrial Waste Waters," His Majesty's Office, London, 1918.
37. Stone, R., *Sewage & Ind. Wastes*, **23**, 1025 (1951).
38. Wise, R. S., *Prac. Inst. Chem. Eng.*, **27**, 101 (1931).

Index

- Acetone
 - from fermentation process, 113
 - in steel pickling waste, 277
- Acid, pickling, 255, 442
 - see also Pickling waste liquor
- Acid mine drainage, 317, 326
 - anthracite, 341
 - bacteria in, 338
 - cause of, 334
 - effects of, 344
 - and stream pollution, 345, 353
 - from strip mines, 343
 - treatment of, 345, 353
- Acid sludge, see Sludge, acid
- Acid values, 258, 260
- Acid wastes, 4, 6, 232
 - and aquatic life, 242
 - characteristics of, 232, 233, 239, 240
 - neutralization of, 244
 - in petroleum industry, 437
 - recovery of, 234
 - and sewerage systems, 239
 - sources of, 232
 - from steel pickling, 255, 442
 - and streams, 242
 - treatment of,
 - by equalization, 236
 - by reduction of strength and volume, 235
 - by segregation, 235
 - see also Acid mine drainage
- Activated sludge process
 - and acid waste, 241
 - for ammonia waste liquor, 390, 391
 - for laundry waste, 472
 - for milk waste, 47
 - for meat waste, 95
 - for pulp mill waste, 203
 - for radioactive wastes, 463
- Aeration, 6
 - of ammonia waste liquor, 406
 - of milk waste, 41
 - of sulfite waste liquor, 204, 206
 - tank, 43
- Alcohol, 111, 113
 - from sulfite waste liquor, 205
 - see also Grain distilleries
- Algae, 10, 16
- Alkaline agents, 6
 - basicity factors of, 258, 271
 - choice of, 270
 - costs of, 271
- Alkaline wastes, 4, 6
 - in petroleum industry, 440, 442, 443
- Alum, coagulant, 148, 157, 158, 184, 185, 456
- Aluminum chloride, in petroleum waste, 437, 440
- American Iron and Steel Institute, 276
- American Leather Chemists' Assoc., 162, 163
- Ammonia
 - from coke oven, 354, 364, 366
 - as neutralizing agent, 244
 - in sulfite pulp process, 207
- Ammonia waste liquor, 366
 - activated sludge treatment for, 390, 391
 - biological treatment of, 385, 395
 - BOD of, 367, 368, 370
 - composition of, 366
 - phenol in, 390, 391, 398
 - toxicity of, 367, 370
 - treatment with anaerobic organisms, 391
 - treatment with sewerage, 386, 387, 390, 391
 - see also Coal carbonization waste
- Ammonium sulfate
 - from coal carbonization, 365, 376
 - from pickle liquor, 276, 279
- Amylase waste, 128
- Anthracene, from coal tar, 382
- Anthracite mines, 327, 341
- Anthrax, from tanning waste, 148
- Antibiotics
 - from grain stillage, 105
 - waste from, 126, 127
- Armco Steel Corp., 408

- Arsenic, 148
- Atomic bomb, 452
- Atomic Energy Commission, 450
- Aureomycin, 127
- B_{12} fermentation waste, 128
- Bacitracin, 127
- Bacteria
 - in acid mine drainage, 338
 - and phenol destruction, 386, 389, 392
 - physiological activity of, 11
 - pollutional, 9, 26
 - and stream purification, 11, 26
- Bacteriophage, 28
- Basicity factors, 246, 258
 - and acid value, 260
 - of alkaline agents, 271
 - determination of, 258, 259
- Beer, *see* Brewing
- Beet sugar
 - manufacture, 473
 - wastes, 474, 475
 - reduction of, 476
 - treatment of, 477
- Belle Center Creamery and Cheese Co., 49
- Benzene process, 398
- Benzoic acid, 393
- Biochemical oxygen demand, 3
 - of ammonia waste liquor, 368, 370
 - for canning waste, 58
 - tests for, 18, 20
- Biological filtration
 - of ammonia waste liquor, 385, 386, 395
 - of canning waste, 65
 - of laundry waste, 472
 - of meat waste, 95
 - of milk waste, 43
 - of phenolic waste, 385, 391, 407
 - of textile wastes, 185
- Bituminous Coal Research, Inc., 320, 339
- Bituminous mines, 331
- Bleachery wastes, 227, 228
- Blood, from meat waste, 92
- Blood worms, 10
- BOD, *see* Biochemical oxygen demand
- Brandy, *see* Wine
- Brewers' grains, 116
- Brewing process, 115
 - by-products of, 115
 - waste from, 118
 - yeast recovery in, 117
- Brines, 4
 - see also* Oil field brines
- Bromine, from oil field brine, 420
- Brookhaven National Laboratory, 451, 456, 462
- Butadiene, 480
- Butanol-acetone stillage, 113, 114
 - feed from, 114
 - waste from, 114
- Buttermilk, 35
- Butyl alcohol-acetone stillage, 113, 114
- By-product recovery, 5
- Calcium base, in sulfite pulp process, 207
- Calcium chloride, 180, 431
- Calcium gluconate waste, 128
- Calcium hypochlorite, for treating wool-scouring wastes, 178
- Calcium oxide, alkali equivalent, 258
- Calcium sulfate
 - limited solubility of, 244, 245, 259
 - from molasses stillage, 113
- Calco Chemical Co., 246
- Cane sugar waste, 478
- Canning industry, 51, 52
- Canning wastes, 51
 - ensilage stack liquor in, 76
 - fish, 485
 - treatment of, 56
 - by biological filtration, 65
 - by chemical precipitation, 60
 - cost of, 77, 78
 - by lagoons, 72
 - at municipal plants, 67
 - by screening, 59
 - by soil absorption, 71
 - utilization of, 79
 - volume of, 57
- Carbazole, 383
- Carbon, activated
 - from molasses stillage, 113
 - as solid absorbent, 404
- Carbon dioxide
 - coagulant for tannery waste, 157
 - and fish life, 29
 - from gassy mines, 317
- Carbon monoxide, from gassy mines, 317
- Casein whey, 36
- Catabolic processes, 12
- Catechol, 394, 400
- Caustics, *see* Alkaline wastes

- Cellulose acetate rayon, 192
- Centrifuges, 6
- Cerium
 - absorption on clay, 461
 - removal by co-precipitation, 456, 457
 - removal by exchange resins, 462
- Chamois, 148
- Chemical precipitation, *see* Chemical treatment
- Chemical treatment
 - of canning waste, 60
 - of kraft mill waste, 200
 - of laundry waste, 472
 - of meat waste, 94
 - of phenolic waste, 408
 - of radioactive waste, 456
 - of tanning waste, 157
- Chicken packing waste, 484
- Chlorine
 - for odor control, 41
 - for phenol removal, 397, 409
 - for tannery waste treatment, 160
 - for wool-scouring waste treatment, 175, 184
- Chlorine dioxide, 397, 409
- Chloromycetin, 127
- Chlorophenols, 393
- Chromate, in plating waste, 288, 295
- Chromium, 151
- Citric acid fermentation, waste, 127
- Citrus waste
 - from canning, 65, 66
 - feed from, 82
- City of Coventry Corp., Gas Dept., 395
- Clays, natural, 461
- Coagulants, 6
- Coagulation, *see* Chemical treatment
- Coal
 - carbonization of, 358
 - see also* Coal carbonization industry, Coal carbonization wastes
 - mining, 312, 315
 - wastes, 317, 326
 - see also* Acid mine drainage
 - preparation wastes, 320
 - production figures for, 313
 - sulfur material in, 336
- Coal carbonization industry, 353
 - by-products of, 353, 355, 362, 364, 377, 381, 382, 383
- Coal carbonization industry (*Cont'd*)
 - procedures in, 358
 - production figures for, 355
 - wastes from, *see* Coal carbonization waste
- Coal carbonization waste
 - acid sludge in, 373
 - ammonia from, 364
 - anthracene from, 382
 - BOD of, 370
 - hydrogen sulfide from, 377
 - naphthalene from, 381
 - nitrogenous aromatic bases from, 381
 - oily, 379
 - phenols in, 383
 - tar from, 364
 - toxicity of, 370, 388
 - see also* Ammonia waste liquor, Phenolic waste
- Coal gas, 354
- Coal mines
 - anthracite, 327, 341
 - bituminous, 331
 - drainage from, 326, 343
 - see also* Acid mine drainage strip, 343
 - waste in, 317, 326
- Coal tar, 364, 383
- Coffee waste, 485
- Coke, 354
- Coke oven industry, *see* Coal carbonization industry
- Color, 10
 - of pulping waste, 226, 229
 - of tanning waste, 148
- Columbium, 461
- Copperas
 - in cement, 276
 - iron oxide pigments from, 275
 - from pickle liquor, 257, 272
 - for sewage treatment, 272
- Co-precipitation, *see* Chemical treatment
- Corn oil, 134
- Corn starch processing, 133
 - by bottled-up method, 134
 - flow sheet for, 135
 - history of, 132
 - products from, 132, 134
 - treatment of wastes from, 137, 138
 - by wet-milling, 133

- Corn syrup waste, 134
- Cotton, 185
 - bleaching, 187
 - printing and finishing, 190
 - processing wastes, 188
 - treatment of, 190
- Creosote oils, 383
- Cresols, 393
- Crude oil, 419, 435
 - see also* Petroleum wastes
- Crystallization, 467
- Cuprammonium rayon, 192
- Curbay BG, 114
- Cutting oil waste, 483
- Cyanides
 - in coke plant waste, 388, 389
 - in plating wastes, 288, 291, 299
- Decontamination unit, 466
- Dehydration waste, *see* Canning waste
- Deinking waste, 214
 - analysis of, 216
 - sludge in, 217
 - treatment of, 216
- Deoxygenation, *see* Biochemical oxygen demand
- Dephenolization, 397
 - by absorption countercurrent liquid extraction, 398
 - by adsorption on solid media, 403
 - for dephenolization effluents, 405
 - efficiency of, 404
 - by vapor-phase dephenolization, 404
- Dept. of Scientific and Industrial Research Board, 193
- Detention tanks, 237
- Detergent wastes, 484
- Diatoms, 16
- Dilution, chemical, 454
- Dilution water
 - of radioactive wastes liquids, 454
 - and stream purification, 17
- Distillers' dried grains, 101
 - see also* Distillers' feeds
- Distillers' dried grains with solubles, 101
- Distillers' dried solubles, 101, 105
 - see also* Distillers' feeds
- Distillers' Feed Research Council, Inc., 100, 104
- Distillers' feeds, 100, 101
 - analysis of, 103, 105
- Distillers' feeds (*Cont'd*)
 - from beer, 117
 - from molasses, 112, 113
 - recovery of, 101, 104
 - uses for, 103
 - wastes from, 107
 - from wine pomace, 124
- Dow Chemical Co., 392
- Dried fermentation solubles, 114
- Drilling muds, 419
- Drum washings, 483
- du Pont de Nemours and Co., Inc., E. I., 406
- Edible oil wastes, 168, 169
- Electrodialysis, 467
- Electrolytic separation, 467
- Emscher tank filter, 388
- Emschergenossenschaft, 399
- Ensilage stack liquor, 76
- Ethyl alcohol, 111, 113
 - from sulfite waste liquor, 205
 - see also* Grain distilleries
- Evaporation
 - of radioactive waste liquid, 454
 - of sulfite waste liquor, 205
- Explosives wastes, 251, 253
- Farbenindustrie, I. G., 399, 400
- Fat processing, *see* Edible oil wastes
- Fats, from edible oil and soap wastes, 169
- Fatty acids, from edible oil and soap wastes, 169
- Feed
 - from antibiotic fermentation waste, 127
 - from corn starch process, 132, 134
 - from grain distilleries, 99
 - from sulfite waste liquors, 204
 - from wine residues, 124
 - yeast, 204
- Fermentation industries, 99
- Ferric chloride
 - from pickle liquor, 278
 - for tannery waste treatment, 159
- Ferric sulfate
 - from pickle liquor, 274, 281
 - for sewage treatment, 274
- Ferron, from pickle liquor, 275
- Ferrous sulfate
 - in pickling liquor, 255, 273, 277
 - as sewage coagulant, 257

- Fertilizer
 production waste, 485
 from tannery waste, 163
 from winery waste, 121
- Fields Point Mfg. Corp., 178
- Filtration, biological, *see* Biological filtration, Trickling filters
- Fish
 and acid wastes, 242, 344
 canning waste, 485
 harmful effects on, 29
 and toxic substances,
 in ammonia waste liquor, 367, 371, 372, 388
 in plating waste, 291, 292, 307
 in pulp mill waste, 199
- Flax, 193
- Flax pulping waste, 221
- Fleischmann Yeast Co., 120
- Flotation processes, 6
 for laundry waste sludge, 472
- Flue gas
 for caustic waste treatment, 442
 for tannery waste treatment, 157, 159
- Formaldehyde wastes, 485
- Freezing, *see* Canning industry
- Frick Coal Co., 347
- Fungi, 16
- Furfural, in petroleum waste, 443
- Gale separator, 380
- Gary Sewerage Commission, 391
- Gasses, toxic
 in mines, 317
 in sewers, 241
- Gas Light and Coke Co., 401
- Gasworks, *see* Coal carbonization industry
- Geiger-Mueller counter, 468
- Gelatine waste, 485
- General American Transportation Corp., 396, 483
- General Motors Corp., 299
- Glen Alden Coal Co., 330
- Glue waste, 485
- Gluten feed, 134
- Glycerol, from grain stillage, 111
- Grain distilleries, 99
 by-product recovery in, 101
 operation of, 101, 102
- Grain stillage, 99, 101
 feed from, 101, 102
 treatment and disposal of, 105
- Grapeseed oil, 121
- Grease
 from meat waste, 92
 sludge, 176
 from tannery waste, 153
 from wool waste, 175, 178, 182, 183
- Grinding oil, 483
- Grit chambers, 41, 477
- Gum wastes, 481
- Hair, 153
- Ilides
 cleaning of, 143
 pickling of, 147
 tanning of, 142, 145, 147
- Hiram Walker and Sons, Inc., 101, 107
- Holley-Mott process, 401
- Hops, brewers', 116
- Hormel Packing Co., 94
- Howard process, 206
- Hydrofluoric acid, 232, 437, 439
- Hydrogen cyanide, 293, 301
- Hydrogen peroxide, bleaching agent, 188
- Hydrogen sulfide
 from coal carbonization, 377, 378
 from petroleum waste, 444
- Illinois Steel Co., 355
- Imhoff tanks, 391
- Industries, waste-producing
 consumption of water by, 2
 distribution of, 1
 population equivalents of, 3
- Inorganic wastes, 4, 24
- Instill process, 376
- Institute of Meat Packing, 93
- Iodine, from oil field brine, 420
- Iodine¹³¹, 460
- Ion exchange, 406, 474
- Iron, electrolytic, from pickle liquor, 275
- Iron oxide
 from pickle liquor, 274
 pigments, 275
- Iron powder, from pickle liquor, 275
- Iron salts, chemical coagulant, 157, 185
- Iron sulfates, as cement, 276
- Irrigation, land, 40, 71
- Isobutyl acetate, solvent, 399

- Isoquinoline, 383
- Jute pulping waste, 221, 223
- Kaiser-Frazer Corp., 299
- Knolls Atomic Power Laboratory, 455
- Koppers Co., 382, 383, 390, 399, 400, 403
- Koppers vacuum activated process, 377
- Koppers vapor-phase dephenolizer process, 404
- Kraft mill waste, 195
 - BOD of, 198
 - composition of, 198
 - effect on streams, 195
 - lagooning of, 200
 - sources of, 197
 - toxicity of, 197, 199
 - treatment of, 199
 - chemical, 200
- Kraft pulp process, 195, 196
 - see also* Kraft mill waste
- Kuhner Packing Co., 95
- Lactic acid fermentation waste, 128
- Lagoons
 - for acid waste equalization, 237
 - for cannery waste, 72
 - for edible oil wastes, 169
 - for pulp mill waste, 199, 206
 - sludge, 160
 - for tannery waste, 160
- Lancaster Iron Works, 48
- Land irrigation, 40, 71
- Lanthanum, 462
- Laundry wastes, 471
 - analysis of, 471
 - radioactive, 463
 - treatment of, 472
 - see also* Soap waste
- Lawrence Experiment Station, 174
- Leather finishing, 145
 - see also* Tanning, Hides
- Legislation, on pollution, 4
- Light oil process, 398
- Lime
 - basicity factor of, 244
 - as neutralizing agent, 159, 160, 184, 200, 244, 253, 258, 262, 264, 267
 - sludge, 477
 - from tanning waste, 153
- Limestone, 244, 246, 267
- Limestone beds, 249
- Liquid wastes, 4
 - see also* Ammonia waste liquor; Pickling waste liquor, Plating wastes, Sulfite waste liquor
- Los Alamos, 459, 463
- Lowenstein-Lom process, 401
- Lucky Lager Brewing Co., 119
- Magdeburg "P-process", 389
- Maggots, rat-tail, 10
- Magnesia
 - from dolomite, 279
 - in sulfite pulp process, 207
- Magnesium, from oil field brines, 420
- Magnesium oxide, low solubility of, 264
- Mallory process, 47
- Manganese concentrate, 278
- Manganese dioxide, 409
- Manganese ores, 409
- Margarine wastes, 168, 169
- Mellon Institute of Industrial Research, 276, 318, 349
- Microorganisms, *see* Bacteria
- MPC values, of radioisotopes, 469
- Mead Johnson Co., 47, 48
- Meat industry, 87
- Meat wastes, 89
 - analysis of, 91
 - BOD of, 92
 - pollutional effects of, 92
 - recovery of, 92
 - treatment of, 93
 - biological filtration, 95, 96
 - chemical, 94
 - with municipal sewage, 96
 - sedimentation, 93
- Methane, from gassy mines, 317
- Metallgesellschaft, A. G., 400
- Metzner process, 123, 124
- Milk and by-products
 - BOD of, 33
 - waste from, *see* Milk products waste
- Milk industry
 - operations of, 31
 - waste in, *see* Milk products waste
- Milk plant, 31
 - standard maximum load of, 38, 39
 - waste, *see* Milk products waste
- Milk products waste, 31
 - by-product utilization of, 35

- Milk products waste (*Cont'd*)
 disposal of, 34
 prevention of, 33
 from rinsings and washings, 37
 sources of, 33
 treatment of, 39
 by activated sludge process, 47
 by aeration, 41
 by biological filtration, 43
 by land irrigation, 40
 by screen and grit chambers, 41
- Milwaukee, Wisconsin, Sewerage Commission, 390
- Mines, *see* Coal mines
- Molasses stillage, 111
 by-products of, 113
 uses for, 112
 waste from, 113
- Morse separator, 380
- Municipal plants, *see* Sewage
- Naphthalene, from coal tar, 381
- National Canners' Assoc., 73
- National Radiation Protection Committee, 469
- National Yeast Corp., 120
- Neutralization, 6, 270
- Neutralizing agents
 for acid wastes, 6, 244, 245, 270
 for alkaline waste, 6, 440, 443
 for pickle liquor, 270, 271
- Niobium, 461
- Nitrogen salts, 200
- Nitroglycerine, 253
- Nuclear bombs, 452
- Nuclear reactors, 451
- Nylon, 192
- Oak Ridge National Laboratory, 451, 456
- Odor, 41, 481
- Ohio River Pollution Control Report, 362
- Ohio River Valley Water Sanitation Commission, 408
- Ohio State Health Dept., 408
- Oil, 4
 acid, 441
 from coke-oven processes, 379, 380
 crank-case waste, 448
 crude, 419, 435
 see also Petroleum waste
- Oil (*Cont'd*)
 cutting and grinding, 483
 edible, 168, 169
 Oil field brines, 29, 420
 Oil separators, 447
 Oregon State College, 207
 Organic material, 6
 Oscar Mayer plant, 91
 Oxidation, 6
 Oxygen
 demand, *see* Biochemical oxygen demand
 dissolved in stream, 18, 29
 Oxygen sag curve, 22
 Oxygen sag method, 20
 Ozone, 409
- Paper machining wastes, 208
- Paper mills, *see* Pulp mill waste
- Penicillin wastes, 126
- Pennsylvania Sanitary Water Board, 321, 350
- Pennsylvania State Health Dept., 163
- Pequanoc Rubber Co., 397
- Petroleum industry, 419
 wastes in, *see* Petroleum wastes
- Petroleum wastes, 419
 acid-containing, 437
 caustic-containing, 440
 chemical-containing, 443
 condensate water, 435
 cooling water, 446
 from crude oil handling, 419
 gases, 444
 oil-containing, 424, 429
 from refining, 422, 427, 428
 slop oils, 426
 sludges and solids, 426, 445
 from transportation and marketing, 447
- pH, control equipment, 247
 and fish life, 29
- Phenanthrene, from coal tar, 382
- Phenol, 383
 and bacteria, 392
 in petroleum waste, 437, 441
 recovery processes, 397
 removal of, 385, 405, 410
- Phenolic wastes, 383, 437, 441
 treatment of, 385, 405
- Phenosolvan process, 399
- Phosphate, coagulant, 457

- Phosphate "P-process," 389
Phosphates waste, 485
Phosphoric acid, 437, 440
Phosphorus, radioactive (P^{32}), 463
Phosphorus salts, 200
Phthalic anhydride, from naphthalene, 382
Pickling waste liquor, 255
 analysis, 258
 by-products from, 272
 disposal, 256
 with sewage, 257
 neutralization treatment, 256
 agents for, 270
 from stainless steel, 281
 use for, 442
Picoline, 383
Pitch, 384
Plating baths, 285
Plating wastes, 283, 288
 cyanide-containing, 288, 291, 299
 effects on streams and sewers, 291
 sources of, 287
 strength of, 288
 treatment of, 290, 293, 299
Plutonium, 456, 459, 463
Poisons, *see* Toxic substances
Pollution, stream
 by sewage, 8
 by industrial wastes, 10
Pomace, grape, 123
Ponding, 406, 477
Population equivalents, by industries, 3
Post-dephenolization, 405
Potash
 from molasses stillage, 113
 from wool-seouring waste, 175
Potassium permanganate, 409
Pott-Hilgenstock process, 399
Powder, smokeless, 252
Precipitants, 6
Precipitation, *see* Chemical treatment
Protozoa, 17, 27
Pulp mill waste, 194, 228
 bleachery, 227
 deinking, 214
 kraft, 195
 paper machine overflow, 208
 rag, rope jute, and flax, 221
 semi-chemical, 244
 soda, 201
Pulp mill waste (*Cont'd*)
 strawboard, 217
 sulfite, 201
Pyridine, from by-product coke, 383
Quinoline, 383
Radioactive wastes, 450
 constituents of, 452
 health hazards of, 467
 instrumentation of, 468
 MPC values of, 468, 469
 in sewerage systems and streams, 453
 sludge disposal for, 467
 sources of, 450
 treatment and disposal of, 452, 454
Radioactivity, 468
Radioisotopes
 disposal of, 451
 mixtures of, 453, 457
 use of, 451
Radium-226, 452
Rag pulping waste, 221, 223
Rayon, 191, 192
Recirculating filter, 44
Residues, from treatment of waste, 7
 see also Sludge
Resins, synthetic, 462
Riboflavin fermentation waste, 128
Rope pulping waste, 221, 223
Rubber wastes, 479
 from mfg. of rubber articles, 479
 reclaimed, 480
 synthetic, 480
 analysis of, 481
 treatment, 481
Ruthenium, 456, 463, 466
Sand filters, 96, 466
Sand washing, 485
Schönburg "Tri-process," 389
Screens, 41, 59, 477
Sedimentation
 of meat waste, 93
 and stream purification, 18
 of tanning waste, 155
Self-purification, test for, 20
Settling tanks, 477
Sewage, municipal
 and ammonia waste liquor, 367, 386,
 387, 390, 391
 and canning waste, 67

- Sewage, municipal (*Cont'd*)
 and corn starch waste, 137, 138
 effect on streams, 8, 9
 and laundry waste, 472
 and meat waste, 96
 and phenolic waste, 386, 390, 391
 and pickling waste liquor, 257
 and plating waste, 291
 and pulp mill waste, 203
 and tanning waste, 153
Silica-Gel process, 376
Silk, 191
Simonsen-Mantius process, 375
Skim milk, 35
Slaughterhouse wastes, *see* Meat wastes
Sludge, 6, 7
 acid, 373, 376, 438, 445
 from ammonia waste liquor, 373, 376
 from beet sugar waste, 478
 index, 49
 from laundry waste, 472
 lime, 477
 oil, 434
 from petroleum waste, 438, 445
 from radioactive waste, 467
 in streams, 25
 from tanning waste, 160
 see also Activated sludge process
Sludge worms, 10
Soap processing waste, 168, 472
Soda base, in sulfite pulp process, 207
Soda mill waste, 201
Soda pulping wastes, 201
Sodium carbonate, neutralizing agent, 244
Sodium dichromate, 409
Sodium hydroxide
 neutralizing agent, 244
 recovery of, 234
Sodium hypochlorite, 41, 188
Sodium nitrate, 72, 73, 74
Sodium peroxide, 409
Sodium sulfate, from pickle liquor, 278
Sod oil, 148
Soil absorption, *see* Irrigation, land
Solids, 6
Solvay Process Co., 354
Special Liquid Curbay, 112
Stack gases, 444
Steel pickling wastes, 255
Steffens' process, 474
Stevenson process, 375
Stillage
 grain, 99
 BOD of, 101
 pollution load of, 107
 recovery of feed from, 101
 treatment and disposal, 105
 uses of, 105
 molasses, 112
 wine, 124
Strawboard waste, 217
 analysis of, 218
 stream pollution by, 218
 treatment of, 219
Streams, acid mine drainage in, 345
 acids in, 242
 and bacteria, 27
 explosives waste in, 253
 pollution of, 2, 8, 10, 28
 self-purification of, 11, 23, 24
 sulfite waste liquor in, 206
Streptomycin, 127
Strontium, 456, 457, 461
Styrene, 480
Sugary wastes, 479
 see also Beet sugar waste, Corn sugar waste, Corn syrup waste, Molasses stillage
Sulfate mill waste, *see* Kraft mill waste
Sulfides, in oil condensate wastes, 435
Sulfite pulp process, 201, 202
Sulfite waste liquor
 BOD of, 203
 by-products from, 122, 204, 205
 composition of, 201
 lagooning of, 206
 treatment and disposal of, 203
 yeast from, 122
Sulfur
 from acid sludge, 438
 from hydrogen sulfide, 378, 444
 from sulfur dioxide, 444
Sulfuric acid
 from acid sludge, 234, 375, 438
 as acid waste, 232
 from coal carbonization waste, 375
 from hydrogen sulfide, 377, 444
 from pickle liquor, 273, 274
 from petroleum waste, 439
 strength of, 244
 for waste treatment, 157, 158, 175, 178, 255, 437

- Suspended matter, 29
- Sweet potato starch waste, 485
- Synthetic fibers, 192
- Tank car washings, 482
- Tanks
 - aeration, 43
 - coagulation, 477
 - detention, 237
 - settling, 477
- Tanners' Council of America, 142
- Tannin, from grape pomace, 124
- Tanning
 - agents, 142
 - with alum, 148
 - with chrome salts, 146
 - with oil, 148
 - with vegetable tannins, 143
 - wastes, 148
- Tanning wastes, 148
 - analysis of, 149, 150, 151, 152
 - characteristics of, 148
 - disposal with sewage, 153
 - plants for, 163, 164
 - recovery of, 153
 - treatment of,
 - by chemical precipitation, 157
 - secondary, 162
 - by sedimentation and storage, 155
- Tar, 364
- Tar acids, 383, 388
- Tartrates, from wine residues, 123, 125
- Taste, 9, 10, 481
- Terramycin, 127
- Tetraethyl lead, 448
- Textile processing wastes, 171
 - see also* Wool, Cotton, Silk, Rayon, Synthetic fibers
- Thiocyanates, 385
- Thiosulfates, 388
- Thorium-232, 452
- Thylox process, 377
- TNT, 251
- Tovrea Packing Co., 94
- Toxic substances, 6, 24
 - in ammonia waste liquor, 367, 388
 - and fish life, 29
 - in plating waste, 291
 - radioactive, 469
- Treatment of wastes, basic principles of, 6
- Trickling filters
 - for cannery waste, 65, 66
 - for laundry waste, 472
 - for meat waste, 95
 - for pulp mill waste, 203
 - for radioactive waste, 464
 - for sugary waste, 479
- Trieresyl phosphate process, 399
- Trinitrotoluene (TNT), 251
- Turbidity, 8, 10
- Turpentine, from kraft and soda mills, 230
- Ufer process, 376
- U.S. Bureau of Mines, 341
- U.S. Citrus Products Laboratory, 81
- U.S. Public Health Service, 2, 393, 394, 408
- United States Steel Co., 358, 391
- University of California, College of Agriculture, 81
- Uranium-238, 452
- Vacatone, 112
- Vanillin, from sulfite waste liquor, 207
- Vinyon, 192
- Viscose rayon waste, 191
- Vitamin B, from grain stillage, 105
- Water
 - bacteria in, 9, 11
 - color, 10, 148, 149
 - consumption by industries, 2
 - cooling, 446
 - mine, 327
 - odor, 9
 - oil-containing, 429
 - organisms in, 12, 16, 17
 - self-purification of, 11
 - taste, 9, 10
 - turbidity, 8, 10
 - see also* Streams
- Western Pennsylvania Coal Operators Association, 318
- Western Regional Research Laboratory, 81
- Whey, 36
- Wine
 - production, 122
 - residues, 123

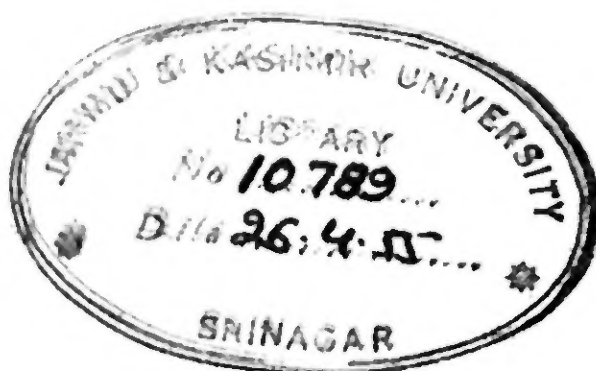
Wine (*Cont'd*)

- stillage, 124
- tartrates from, 123
- Wine Institute, 124
- Winslow Bros. and Smith, 157, 160
- Wisconsin State Board of Health, 73
- Wood, processing for pulp, 194
- Wool, 171
 - dyeing and finishing waste, 184
 - treatment of, 185
 - scouring waste, 172, 183
 - treatment of, 173, 183

Wool fat, 175

Yeast

- feed, 204
- growth stimulant, 105
- from molasses stillage, 113
- production waste, 120
- recovery in brewing, 117
- from sulfite waste liquor, 122, 204
- Yttrium, 456, 457, 459, 461
- Zinc chloride, 437
- Zirconium 461



ALLAMA IQBAL LIBRARY



10789